AAMRL-TR-89-008

CONFERENCE ON OCCUPATIONAL HEALTH ASPECTS OF ADVANCED COMPOSITE TECHNOLOGY IN THE AEROSPACE INDUSTRY

VOLUME II. PROCEEDINGS

MARCH 1989

PROCEEDINGS FOR THE PERIOD 5-9 FEBRUARY 1989

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HARRY G. ARMSTRONG AEROSPACE MEDICAL RESEARCH LABORATORY
HUMAN SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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AAMRL-TR-89-008
Volume II

This summary represents the statements and opinions of the participants and does not necessarily reflect the policy or position of the Department of Defense and the separate services, the Suppliers of Advanced Composite Materials Association (SACMA), the Aerospace Industries Association (AIA), or the member companies of these organizations.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

MICHAEL B. BALLINGER, Lt Col, USAF, BSC
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SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION AVAILABILITY OF REPORT Approved for public release, distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) AAMRL-TR-89 008
6a. NAME OF PERFORMING ORGANIZATION NSI Technology Services Corporation 6b. OFFICE SYMBOL (if applicable)	7a NAME OF MONITORING ORGANIZATION AAMRL, Toxic Hazards Division
6c. ADDRESS (City, State, and ZIP Code) 101 Woodman Dr., Suite 12 Dayton, Ohio 45431	7b. ADDRESS (City, State, and ZIP Code) HSD, AFSC Wright-Patterson AFB, Ohio 45433
8a. NAME OF FUNDING/SPONSORING ORGANIZATION 8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F33615-85-C-0532
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
62202F	6302	00	01

11. TITLE (Include Security Classification)
CONFERENCE ON OCCUPATIONAL HEALTH ASPECTS OF ADVANCED COMPOSITE TECHNOLOGY IN THE AEROSPACE INDUSTRY: VOLUME II PROCEEDINGS

12. PERSONAL AUTHOR(S)

13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
PROCEEDINGS	FROM: 5 Feb 89 TO 9 Feb 89	March 1989	414

16. SUPPLEMENTARY NOTATION
This report was prepared with the cooperation and editorial assistance of Battelle, 505 King Avenue, Columbus, Ohio, 43201-2693, a subcontractor to NSI Technology Services Corporation.

17. COSATI CODES			18. SUBJECT TERMS (Continued on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	advanced composite materials; industrial hygiene; resins; composite materials; methylenedianiline; fibers; prepregs;
06	11		
11	04		

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
The U.S. Air Force sponsored a national conference on the Occupational Health Aspects of Advanced Composite Materials in the Aerospace Industry, 6-9 February 1989, in Dayton, Ohio. The conference was developed in cooperation with the Suppliers of Advanced Composite Materials Association (SACMA) and the Aerospace Industries Association (AIA). It was attended by over 230 representatives from the Department of Defense and the Service Components, industry, labor, and other Federal agencies.

The goals of the conference were to promote technology transfer and to provide a forum for discussion to determine
- What is known and, possibly more importantly, what is not known about the health effects of composites.
- Availability and effectiveness of current controls in preventing worker illness.
- The need for epidemiologic studies on the health effects of composite materials.
- The availability of health information to the worker in the form of training and hazard communication.

The overall conclusion is that while there are some health problems associated with the use of these materials, the problems are neither unique to these materials nor the aerospace industry, and the problems are solvable with current technology.

The report on the conference is provided in two volumes. Volume I Executive Summary includes summaries of the major issues addressed by the conference along with abstracts of the technical presentations. Volume II Proceedings provides the full text of the presentations. Keywords:

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTIC USERS	UNCLASSIFIED

22. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
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DD FORM 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

PREFACE

A conference on Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry was held in Dayton, Ohio, on 6-9 February 1989. The Air Force Systems Command's Human Systems Division, Harry G. Armstrong Aerospace Medical Research Laboratory (AAMRL) hosted the conference which was sponsored by the Department of the Air Force with the cooperation of the Suppliers of Advanced Composite Materials Association (SACMA) and the Aerospace Industries Association (AIA). Coordination of the conference was provided by NSI Technology Services Corporation, under the terms of Contract No. F33615-85-C-0532 with the Air Force. LtCol Harvey J. Clewell served as the Contract Technical Monitor.

LtCol Michael B. Ballinger, AAMRL/TH, served as the Conference Chairman, and Patsy J. Gergely served as the Conference Administrator. The Session Coordinators were: LtCol Michael B. Ballinger (Perspectives and Expectations), Dr. David R. Mattie (Technology Overview), Major Robert G. Elves (Health Effects and Exposure Considerations), CDR David A. Macys (Engineering Controls and Work Practices), LtCol William D. Gould (Occupational Medicine Considerations), LtCol Edward C. Bishop (Hazard Evaluation and Communication), and LtCol Harvey J. Clewell (Needs Review and Action Agenda). Lois A. Doncaster, was the Conference Coordinator for NSI Technology Services Corporation, which provided administrative support for the conference. This report was prepared with the technical and editorial assistance of Battelle. In particular, Keith J. Johanns and Barbara S. Bechtel provided key support during the preparation of the consensus statements and summary

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I. CONFERENCE SUMMARY

The U.S. Air Force sponsored a national conference on the Occupational Health Aspects of Advanced Composite Materials in the Aerospace Industry, 6-9 February 1989, in Dayton, Ohio. The conference was developed in cooperation with the Suppliers of Advanced Composite Materials Association (SACMA) and the Aerospace Industries Association (AIA). It was attended by over 230 representatives from the Department of Defense and the Service Components, industry, labor, and other Federal agencies.

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- What is known and, possibly more importantly, what is not known, about the health effects of composites.
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The overall conclusion is that while there are some health problems associated with the use of these materials, the problems are neither unique to these materials nor the aerospace industry, and the problems are solvable with current technology.

The following section summarizes the major issues addressed by the conference and was prepared by the summary working group listed at the end of this chapter. A more extensive summary of the specific topic addressed by each of the conference technical sessions is provided at the beginning of the section containing the papers presented at that session.

- **Advanced Composites Are Critical To National Defense.**

Advanced composites were first introduced in the late 60's and early 70's on the F-111, F-14, F-15, and F-16. Since that time the technology has matured to where 40-60 percent of the next generation fighter and attack aircraft will be made of composite structures The superior specific strength, specific stiffness, and fatigue resistance offered by advanced composites produce increased performance at reduced weight. The increased capabilities they give our aircraft make composites critical to national defense.

- **The Use Of Composites Is Rapidly Increasing.**

Virtually every airframe being designed today is using advanced composites for a portion of its structure. This is true for commercial as well as military aircraft, domestic as well as foreign aircraft. The explosion in the use of this technology is leading to dramatic increases in the quantity of advanced composites processed every year. One domestic airframe company expects to increase its use of composite material in the next decade from 100,000 pounds to over 1,000,000 pounds annually.

- **The Worker Is The Most Important Asset.**

Employers must convince their workers that they are concerned for their workers' welfare and allow the workers to be involved in ensuring a safe working environment. Employees must not only be protected, but also feel protected.

- **The Availability And Quality Of Material Safety Data Sheets (MSDS) Need Improvement.**

The MSDS is the primary source for transmitting hazardous material information from the initial supplier to the worker. Although the supplier is required by the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard (HCS) to supply the MSDS to the user, OSHA enforcement of the HCS effectively shifts the burden of obtaining the MSDS to the user. This requires the user to establish administrative mechanisms to ensure the MSDS is available to the worker.

Quality of MSDS information is also a major issue. There is a large degree of variability in the quality and format of information from various manufacturers. Often this information is written in highly technical language which is not readily understood by the target audience, the worker.

- **Medical Monitoring Is A Component Of An Effective Occupational Medicine Program.**

Medical monitoring is an important tool to provide early identification and prevention of occupational illness. Available technological advances offer new levels of effectiveness, but the rapid proliferation of industrial chemicals challenges medical analytical capabilities.

- **Occupational Health Considerations Must Be An Integral Part Of The Design And Manufacturing Process.**

Health and safety professionals must be involved at the initial stage of product development. Their involvement must continue through the entire process of production, marketing, and use. Toxicity assessments and the development of exposure control measures and medical surveillance protocols based on these assessments can progress in parallel with industrial research and development. This will help ensure the information needed by manufacturers and users will be available at the time of product introduction. This proactive "system safety engineering" approach involving supplier, manufacturer, and user health and safety professionals will ensure good control of potential health effects, and will also minimize the impact of controls on production.

- **Technological Advances In Advanced Composite Materials Have Outpaced The Health Issues.**

Although the rapid development of these materials has not always allowed health issues to keep pace with the introduction of new composite systems, there is an underlying awareness of the potential health hazards associated with these materials. The rapid evolution and turnaround of resin matrix systems requiring long-term toxicological studies makes the health hazard evaluation of individual resin systems infeasible. Rather, the hazards associated with individual components of a given resin matrix system have been, and should continue to be, evaluated and used to develop employee health protection.

- **Engineering Controls Are Generally Available And Need To Be Consistently Applied.**

The technology required to control potential hazards that may be associated with composites is generally well understood, available, feasible, and effective. Proper implementation of the controls, however, is key to effective hazard control. Where chemical hazard and toxicologic information is unknown or sketchy, there is a consensus among health professionals that the controls used must be based upon a conservative approach to maximize worker protection. Controls are inconsistently applied in the composites industry. Diversity is seen both in the choice of controls and the effectiveness of the controls used.

- **Personal Protective Equipment Is Frequently Required To Supplement Or Temporarily Replace Engineering Controls.**

Personal protective equipment, while generally available, is not always satisfactory. Issues identified include worker acceptance, impacts on product quality and production rate, lack of uniform performance standards, and inability to make safety or economic changes due to Federal Agency certification requirements. These problems are compounded when inadequate information on the specific hazards is available.

- **Engineering Controls And Work Practices For Repair Are Different For Depot- And Field-Level Repairs.**

The engineering controls and work practices for repairing advanced composite structures at the depot-level are very similar to those that would be found in a manufacturing facility. For field-level repair, however, it is unclear to what extent engineering controls can or must be used. Work practices will probably continue to rely heavily on personal protective equipment.

- **Fibers From Advanced Composites Are Of Minimal Health Risk.**

The health concerns of raw reinforcement fibers are minimal. Numerous studies of these fibers have indicated that they do not pose an asbestos-type hazard.

- **The Health Risk From Composite Material Dust Is Less Well Characterized.**

The health effects of dust generated from machining cured composites are less understood. Preliminary studies indicate that the dusts have very few fibers of respirable size. The particles may be capable of producing a lung response greater than that from "nuisance" dusts but far less than that from quartz dust. The dust may also include uncured matrix material which could increase the health risk.

- **Dermal Contact Is A Significant Route Of Exposure.**

Dermal exposures are considered to be an important problem to address because exposure to the skin may be significant. It is, however, more difficult to evaluate and quantify than inhalation exposures. There is also confusion about the appropriate type of glove or barrier cream which will provide both protection and the required tactile sensitivity. Hand protection must not introduce contaminants into the product which may affect the quality

- **Odor And Discomfort Complaints Should Be Taken Seriously.**

Even though workers may not be experiencing a direct toxic effect due to exposure, complaints of odor and discomfort must be taken seriously. These complaints indicate concerns which, if left unaddressed, in the absence of sufficient health information may become a more serious problem

- **Illness May Be Exacerbated By Misinformation.**

Any adverse health effect related to chemical exposure may be significantly exacerbated by misinformation from health care providers, news media, and poor communication between labor and management.

- **Antibody Testing May Not Correlate With Clinical Disease.**

Testing for antibodies to formaldehyde and most other reactive chemicals currently does not correlate with chemical exposure and chemical disease Such antibody testing should be performed only as part of a well-controlled epidemiologic study.

- **Epidemiologic Investigation Should Be Carefully Considered.**

Epidemiologic investigation of potential health effects of composite materials, such as immunological or neuropsychological dysfunction, should be carefully considered, realizing the inherent limitations of such studies. These limitations include the potential for bias, the difficulty of classifying exposure in a multi-chemical environment, the lack of animal data demonstrating a causal link to a specific adverse effect, and the limited sample sizes of the exposed cohorts.

- **The Cooperative Spirit Fostered By This Conference Should Be Actively Maintained.**

One of the most notable results of this gathering has been the formation of more extensive ties among the representatives of the various government agencies, industries, and labor. Maintenance of these relationships will go a long way toward ensuring the rapid and effective transfer of information as well as preventing duplication of effort. The continued preservation of the safety and health of aerospace workers can best be assured through a common commitment to a coordinated proactive program.

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II. PERSPECTIVES AND EXPECTATIONS

OPENING REMARKS

Major General Fredric F. Doppelt, USAF, MC

Commander, Human Systems Division (AFSC)
Brooks Air Force Base, Texas

Ladies and Gentlemen, I am very pleased to be able to co-host this important national conference along with Mr. Gary Vest, our Deputy Assistant Secretary of the Air Force for Environment, Safety, and Occupational Health.

It is my special privilege to be able to welcome you to Dayton, the "Birthplace of Aviation" and the home of Wright-Patterson Air Force Base.

Wright-Patterson AFB is not only the home of Headquarters Air Force Logistics Command but is also host to Air Force Systems Command's (AFSC) Aeronautical Systems Division and three major components of AFSC's Human Systems Division in the form of our Life Support Systems Program Office, the Armstrong Aerospace Medical Research Laboratory (AAMRL), and the Logistics Support and Human Factors division of our Human Resources Laboratory.

Wright-Patterson AFB thus symbolizes the teamwork necessary Air Force-wide to bring advanced science and technology to bear on the development, acquisition, and life cycle support of advanced weapons systems so vital to our national defense and to assure that these systems continue to maximize the full utility of our most valued asset - that of the human in the system.

This is the mission of AFSC's Human Systems Division: to serve as the weapons system independent advocate of the human in our Air Force systems and to assure that we are capable of realizing the full potential of our highly skilled and professional force in operating and maintaining these systems in an effective and safe manner. Solving the human challenges in Air Force systems and operations is the entire focus of our Human Systems Division, and that is our challenge during this conference.

The title of this conference was carefully chosen to reflect the breadth of the assignment. The "Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry" involve many disciplines, all of which are well represented on our agenda and in the audience.

I challenge the various disciplines that you, the conference attendees, represent to work closely together, not only this week during the conference, but in the future as well. It is our hope that this conference will foster closer professional ties and working relationships between members of these various disciplines in different Air Force commands, between Air Force and other DoD and Government agencies, and with industry and labor.

I have always been a strong advocate of government working together with industry and labor to solve common or related problems. This conference is a splendid example of professional cooperation bringing us together to work more closely on an area of common interest. I hope this spirit of cooperation will continue to extend to all areas of concern between the Air Force and industry to assure full and effective application of our advanced technologies.

Our task at hand this week is to review the entire spectrum of the use of composite materials in the aerospace industry; that is, from the material manufacturer to the airframe assembler and through the maintenance and repair processes.

This technology has been with us for awhile. Many industries have significant experience with these materials. However, the situation may be changing with the increasing use of these materials for ever broader applications.

We should carefully set the stage by looking at the technology base. What are these materials, and how are they made? How does this manufacturing scenario differ from the traditional setting? We are still in the fledgling stages of learning the maintenance and rework challenges posed by composite components of fielded systems. The systems on the immediate horizon may add additional uncertainty simply due to the sheer quantity of the materials involved.

Component materials have been studied for toxic effects and, in general, are not considered high risk materials, but are there data gaps in the area of the synergistic effects of the complex chemical mixtures involved?

Fire and mishaps involving aircraft with composite components may present another challenge. A joint Air Force/Navy Research Program has been recently initiated throughout AAMRL here at Wright-Patterson AFB to study the toxicity of aerospace composite materials combustion products.

You in the audience represent a composite industry that encompasses the entire spectrum of workplace environments. Your individual perspectives on appropriate engineering controls and work practices should be very enlightening and promise to be one of the more fertile areas for information crossfeed.

The occupational medicine physician also occupies a prominent place in protecting the health of the worker. Sharing details on medical monitoring programs as well as clinical experiences from the various workplaces will occupy an entire session.

Each of us in executive and supervisory capacities have a prominent responsibility to safeguard the health of our workforces from undue risk. We must not overlook the value of clear and direct communication with our workforce concerning potential health hazards and their control. Effective worker education and training programs are vital to controlling potential hazards and in allaying the concerns of our people.

Effective communication is also our conference goal. Within the constraints of available time, I invite each of you to use the panel discussions at the end of each half-day session to air your candid opinions and questions. This particular forum is a key element in the overall success of this conference. Sharing the knowns and known unknowns of the health aspects of composite materials should provide a future focus on the unanswered questions for both industry and the military.

I would like to thank the many different industry, government, and labor representatives who have generously contributed their time, support, and expertise to our crowded agenda. I want to especially thank the Suppliers of Advanced Composite Materials Association, or SACMA, and the Aerospace Industries Association, or AIA. Mr. Joe Jackson of SACMA and Mr. Dan Nauer of AIA deserve special thanks for their efforts and the efforts of their staffs in helping to plan the agenda and identify speakers.

The response to this conference has been overwhelming. With your active participation, the quality of the proceedings should attest to the value of the conference.

Welcome again, and thank you for sharing your time and perspectives with us.

KEYNOTE ADDRESS
Air Force

Gary D. Vest

Deputy Assistant Secretary of the Air Force for
Environment, Safety, and Occupational Health, Washington, D.C.

Thank you. Good morning ladies and gentlemen. It is a pleasure to welcome you here today to this national conference on the use of advanced composite materials in the workplace environment. Before I begin my remarks, I would like to first extend my appreciation to the Air Force Surgeon General represented here today by Major General Fredric Doppelt and Brigadier General Rufus DeHart for the outstanding work of their fine staffs for putting this conference together in a very short time frame. I would also like to thank the Suppliers of Advanced Composite Materials and the Aerospace Industries Association for their valued assistance in making this extremely important event possible.

I am pleased to see representatives from the aerospace industry, labor, academia, military services, and other federal government agencies who, like the Air Force, share our interest in the occupational health aspects of composite materials manufacture, use, training, acquisition, testing, and medical support. I assume all of us are here to achieve a better understanding of advanced composite materials and to promote technology transfer on the occupational health aspects of handling these materials. The agenda covers the realm of composite materials management and is intended to give us a better understanding of any potential health hazards and effective protective measure for working with these materials. We must continue to apply scientific capabilities to not only provide advances in new products, but also fulfill our obligation to develop, specify, and use materials and processes which are safe and healthful as we produce, use, and maintain the products.

Many eyes are upon this conference, including officials on Capitol Hill who will evaluate results of this gathering before deciding whether or not they need to inquire on their own about the occupational health effects of composites.

The Air Force has been, is, and will continue to be a major user of many hazardous materials Every day, our installations procure, transport, store, and use materials we need to support our weapons systems. Management and employees have always demanded to know more about the materials commonly used in the workplace and have the right to

expect a healthy and safe working environment. Thus we must face and master the challenge of accomplishing our mission while also being good managers of hazardous materials in the workplace and in the environment. Nevertheless, the complexity of this challenge is placing ever increasing demands on our professionals.

We are not alone in our concern for trying to accomplish the task of worker protection. Congress, private industry, and federal agencies are all working to ensure that our creativity is not only applied to development of new weapon systems to protect our nation, but to protect the health of our skilled labor force, both in and out of uniform. This is no easy task, but is extremely difficult to achieve when you consider the thousands of materials that we use. We need to ensure worker health and environmental effects are considered and evaluated at all levels of the machine/human/environmental interface. We need weapons systems that give our military the edge in combat but not at the expense of our most valuable resource, our people.

In terms of this conference, we need your help to find answers to questions on advanced composite materials regarding possible health effects, handling procedures, personal protection, and training.

There has been much public controversy lately surrounding the potential adverse occupational health aspects of the use of composites in the aerospace industry. Newspaper articles, television coverage, and Congressional inquiries have targeted the Air Force primarily because this technology is becoming more prevalent in our new airframes. Contrary to popular belief, composites are not new. They have been used in building and manufacturing materials for a long time. Nevertheless, questions are being raised about the availability of scientific and technical information on toxicity, cumulative health effects, engineering controls, exposure standards, and medical monitoring efforts.

We must be satisfied that we have the answers to these questions; if they are incomplete, then we must strive to find the answers. I look forward to a very productive conference which provides a forum for disseminating information on questions where answers are available and identifying those areas where additional information is needed.

Composites are very important to the Air Force. Composite technology use will continue to grow in the future. In 1986 alone, the military aircraft market increased its use of composites by 12 percent and higher figures are projected for future aircraft. Most of our front-line aircraft, such as the A-10, B-1, F-15, F-16, F-4, B-52, and several cargo aircraft

already have components made of composites based on carbon or boron. The B-1 bomber, for example, has 1,100 pounds of composites in six large, single-piece bomb bay doors and lesser quantities in smaller components. The use of composites is essential to promote weight savings, reduce fatigue stress, increase tensile strength, and prevent corrosion. Composites will play an ever increasing role in building the Advanced Tactical Fighter (ATF), C-17, new missiles, and the military version of the National Aerospace Plane.

As industry continues to strive for more advanced formulations of composites and resin binders, we need to understand the state-of-the-art in composites technology and its implications to occupational health. As you can see from the agenda, we consider knowledge of what constitutes a composite material, how is it fabricated, and what chemicals are used in the process important to understanding the acute and long-term implications on worker health.

We need to address health effects of composites and update our current knowledge of exposure assessment. The Air Force, like its private sector counterparts, uses many different chemicals which often do not come to us with as much toxicological data as we would like to support exposure assessments. Decision makers need a better understanding of the risks associated with use of alternative materials before using them in future weapons systems. Let's not forget the need for exposure standards without which we could not determine if workplace conditions are safe and healthful or require engineering controls for worker protection.

I would like to focus now on our most valuable resource, our workers. I am proud to say that the Air Force medical service has an outstanding occupational health program which is firmly committed to worker protection. We also work closely with state and federal regulatory authorities to monitor the procurement, use, and disposal of hazardous materials. However, it is difficult to implement the training provisions of the new Hazard Communication Standard or Hazard Waste Disposal laws without quality Material Safety Data Sheets (MSDSs). These documents are vital to our occupational health programs and must be as factual and complete as possible. We simply need to know the hazards associated with the materials if we are to develop effective control strategies and if training programs are to be effective.

We are working hard to constantly improve the quality of our occupational medicine programs. Our qualified teams of industrial hygienists, occupational medicine physicians,

and technicians are capable of assessing the physiological implications of worker exposure and conducting worker surveillance programs. If we determine that data gaps exist with our present knowledge of composite technology, then efforts must be pursued to fill the gap We must continue to monitor the occupational environment for health hazards to prevent illnesses and injuries from occurring.

I share Major General Doppelt's view that your active participation in the conference is vital toward achieving our goals and objectives. We need to be open and receptive to the information shared at this conference. It is important that we use the results of this conference to reach a consensus on the state of the knowledge of working with advanced composite materials. If additional knowledge is required, we face the challenge of obtaining it and determining actions necessary to ensure workers remain protected. The results of this conference are very important to the Air Force and fulfilling our commitment to provide a safe and healthful working environment for our workers.

Thank you and welcome to all of you.

KEYNOTE ADDRESS
Suppliers of Advanced Composite Materials Association

J. David Forest

President, BASF - Structural Materials, Charlotte, North Carolina

The Air Force has asked for, and received, assistance from two industry groups in creating the agenda for this conference and in finding speakers. These two groups are AIA and SACMA. I am chairman of the latter group and will attempt to provide you with an overview from our industries perspective.

SACMA stands for "Suppliers of Advanced Composite Materials Association", and is, as the name implies, a trade association of materials suppliers. We have about two dozen member companies who are engaged in making the fibers, the matrix polymers, and the prepregs that collectively are called advanced composite materials. Our customers include the companies who fabricate components for aircraft and aerospace systems and who are represented by AIA. The companies represented in SACMA are predominantly chemical and petro-chemical companies including, besides BASF, the Du Pont Company, Shell Chemical, Amoco, Hercules, Ciba-Geigy, ICI, Hexcel, and a number of others.

The term "composite materials" is used to describe a number of different kinds of products whose single similarity is that at least two different materials are combined to make a new material which has different properties than the constituents. Concrete is a composite material, for example, since it combines cement and gravel. Most often, however, the general term refers to some kind of plastic reinforced with glass fibers. The term "advanced composite materials" is loosely used to denote a group of materials which have higher performance than reinforced plastics in general. This higher performance can come from the use of newer fibers, such as carbon fibers, or newer plastics, such as polyimides, or simply by careful processing of conventional glass fiber reinforced standard polyester, phenolic, or epoxy resins. If I leave you thinking the boundaries between reinforced plastics, composite materials, and advanced composite materials are fuzzy, you have grasped the situation correctly.

Advanced composite materials usually combine the properties of high strength and high stiffness, low weight, corrosion-resistance, and in some cases, special electrical properties. This combination of properties make advanced composites very attractive for

aircraft and aerospace structural parts. The materials are used in considerable quantities as well for golf club shafts, fishing rods, tennis racquets, racing car bodies, bicycles, medical X-ray tables, robot arms, and racing yachts. The latest winner of the America's Cup yacht race was the "Stars and Stripes" catamaran which was largely constructed of carbon fiber reinforced epoxy composite material. The losing New Zealand boat also used carbon/epoxy material, but that's a different story.

The use of the term advanced composite materials really began in the mid-1960's with the development of boron and carbon fibers. In the past 20 years, these new materials have come from the laboratory stage to a rapidly growing new industry, employing some 20,000 people making the materials and the parts. My prediction is that the use of these materials will continue rapid growth through the year 2015, at which time some 750,000 people will be involved in a $30 billion per year industry. Along this future path lie new applications in commercial and military aircraft, ground and marine defense systems, rapid transit vehicles, industrial machinery, and eventually civil structures such as long-span bridges. One study, for example, suggests that advanced carbon fiber composites are the only feasible materials, from a technical standpoint, which could be used to construct a bridge connecting the mainland of Spain to the island of Gibraltar. The study also points out that such a bridge would require all of the world's carbon fiber production for five consecutive years to build. So don't look for this to happen right away.

North America is the center of production and consumption of advanced composites in the "free-world", with about 60 percent of the demand. The balance of demand is roughly an equal split between Western Europe and Asia, primarily Japan. In North America, about 80 percent of advanced composite usage is in aircraft and aerospace applications. The same is true in Western Europe. In Asia, the major use is recreational and industrial items, since the aerospace industry is still small there.

Advanced composite materials cost more than aluminum, titanium, or steel so the usage is highest in military rather than commercial systems at the moment. Military systems, as you know, are driven by performance more than cost. In today's world, commercial systems are very much cost driven.

It is especially appropriate, therefore, that this conference be sponsored by the Air Force. Not only because the US military is the largest end-user of composite fabricated structures, but because military personnel will be involved in growing numbers in the repair and maintenance of composite structures, which requires handling these materials.

I'd like to speak briefly now about advanced composite materials in the context of their danger to worker health. Advanced composite materials are composed of relatively inert fibers surrounded by a plastic matrix. The matrix polymer is the product of the chemical reaction of several complex organic chemicals. These organic constituents have chemical similarities to body tissue, as do foods and medicines, and a wide variety of household products including shaving cream and nail polish. In the vast majority of cases, workers who produce advanced composite parts use prepreg material. Prepreg (which is short for pre-impregnated) is a thin sheet of fibers with a mixture of the unreacted, organic chemicals required to form the matrix polymer already spread through the fiber sheet in just the right amount. The workers cut patterns from the prepreg sheets and stack them carefully on molds. The result is heated under pressure until the matrix chemicals have reacted (cured) and the part is formed. In general, it is the handling and curing of the unreacted prepreg which gives rise to health concerns. Later, trimming and drilling operations pose minor concerns, mostly with nuisance dust, which are easily controlled.

In the early days of the industry, aircraft were made of wood and doped fabrics put together with adhesives. In those days, it was common for the workers to use unreacted organic chemicals. Then the industry turned to metal, mostly aluminum, as its primary material of construction. Metals arrive at the worker's bench already reacted, and relatively inert. Now, of course, the wheel of time and progress is returning to the use of organic chemicals, through advanced composite materials in aerospace, and new work habits and precautions must be learned again.

I do not believe that advanced composite materials are inherently more dangerous to worker safety than metals. But I do recognize that the dangers between these two types of materials are very different, and that workers need help in understanding how to safely deal with composites. I would hope that one product of this conference would be a resource document outlining worker health concerns and precautions from which safe shop procedures could be drawn. I would also encourage you to look for holes in the health data base which need to be filled so that industry has a roadmap to work with.

The suppliers of advanced composite materials long ago recognized the need to help our customers understand worker safety concerns with these materials. To that end, working through SACMA, the suppliers began collecting and summarizing existing data on health effects and recommended precautions from their member companies in 1986. The resulting compendium, in the form of a health effects white paper, will be published early this year In addition, SACMA and AIA have formed a joint task force to look at health effects, safety procedures, and engineering controls necessary to minimize worker exposure risk to health dangers in using advanced composites.

I'd like to comment briefly on the widely publicized cases of health concern with advanced composites which occurred recently. One instance, you will recall, was at a Boeing shop in the Seattle area where commercial aircraft interior parts were fabricated using glass fiber reinforced phenolic prepreg. This case is interesting from several standpoints. For one, it involves phenolics, which are the oldest plastics around. In fact, if you are as old as I am, you remember the time when Bakelite® (which is a reinforced phenolic) was synonymous with plastic. For another, permissible exposure levels of the constituents of phenolics (phenol and formaldehyde) were established long ago. Boeing tests, as well as university tests and Government tests, of the levels of airborne phenol and formaldehyde in this particular shop all showed results well below the permissible exposure level. And yet, some people who worked there got sick. Boeing has apparently solved the problem at least for now by substituting polyester for phenolic.

The second case involved a Lockheed shop in Burbank, California where classified military aircraft parts were made using a variety of prepregs, but not phenolics This case was more widely publicized because of the secrecy surrounding the hardware and has resulted in worker lawsuits which currently make it difficult to find out much about the circumstances. Press reports of interviews with some of the workers, however, show similarity of reported symptoms to the Boeing case.

These two recent cases are of great concern to both the composite material industry and to the aerospace industry. Were these two instances just aberrations? Or can we expect more such instances around the world? What caused these workers' symptoms? What can be done to minimize the chances of future problems?

Perhaps this conference can shed some light on how we proceed to answer these important questions.

I'd like to mention one final thought on the subject of worker health with advanced composites I think you are all aware that organic complexes can provoke what might be loosely described as allergic reactions in some people. Someone in this room is probably "allergic" to penicillin; someone else is allergic to ragweed (probably more than one, in fact); someone else perhaps to bee venom, and maybe someone has had real trouble after eating soft-shell crab. There is considerable amount of historical evidence that some of the reactive organic chemicals used in composites will, over time, cause a few people to become sensitized and exhibit allergic responses to extremely low levels of exposure. Health exposure levels for chemicals are set based on evidence of direct interaction with tissue, and cannot really account for the indirect effects of allergic response in a "sensitized" individual.

It is possible to greatly minimize the risk of sensitization by pre-screening workers The tests are similar to allergy patch tests and are based on skin response. Very few companies who use composites perform such tests, but I would argue that they should. Many of the symptoms described in the press as exhibited by the Lockheed and Boeing workers resemble allergic responses of sensitized individuals. I do not know that allergic response contributed to these cases, but I suggest it might have. This subject will be discussed in more depth in a later session. I would hope that session would begin the task of outlining a suitable pre-screening test procedure for workers.

In summary, I have tried to give you a picture of an important new class of materials which allow us to construct some things not feasible with other materials, and in the broader case, to improve the performance, durability, and safety of many other products. These new advanced composite materials are rapidly expanding their usage volume and can be expected to continue to do so for another 25 years or so. Advanced composites are based on complex organic chemicals, and so give rise to health concerns and procedures different from those of conventional aerospace materials. New work procedures are required, and workers must be trained in these procedures and the reasons for them I've also suggested that worker screening may well be advisable to minimize the risk of individual sensitization.

I thank you for your attention, and leave you with the charge that this conference is dealing with a serious set of matters which require timely resolution.

KEYNOTE ADDRESS
Aerospace Industries Association

Joseph F. Peritore

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Hello and good afternoon. I want to thank the Air Force for launching this important conference. This is a unique opportunity for us -- the customer, the manufacturers, the material suppliers, and the regulatory agencies to join forces; to share information and ideas; and to step up to the challenges that are facing us as we work to continuously improve the quality of our work environment and products:

- Products that must meet our customer's requirements;
- Products that must be competitive in today's marketplace;
- Products that are designed, built, and serviced by a workforce that is confident in the quality of their work environment.

Today, the aerospace industry is challenged on many fronts: globalization of our industry, intense competition, and the need for large investments in technology to maintain our competitive edge. These are significant issues, and this is not an exhaustive list. But clearly they are factors that shape today's business environment.

But the business environment of today is also shaped by increased concerns about worker health and safety.

We are developing and using complex and toxic materials in the workplace. We must ensure the health and safety of our only strategic resource -- the people who work in our industries and serve in our armed forces.

Competition presses us to shorten the time line between the customer requirement and the completed product I believe that if we address health and safety concerns through a continuous quality improvement process -- a process of working together during the product development cycle -- we can help shorten development time and maintain our competitive edge. This is our challenge -- this is the opportunity the conference presents us with.

The aerospace industry has begun a coordinated effort to review and improve health and safety practices. Working with Suppliers of Advanced Composite Materials Association (SACMA), an Aerospace Industries Association (AIA) ad hoc team is developing an industry-wide plan of action. As we address health and safety concerns, we must recognize today's competitive environment.

This conference is an opportunity to build a consensus for change in our approach to addressing health and safety concerns. Yes, we are here to address a specific industry-wide concern. But we would be missing an opportunity if we left this conference without addressing how we can work together to continuously improve the quality of the work environment.

One of the barriers to improvement is the current role of the health and safety organization. We need to change safety professionals from policemen to consultants. We need to continue to expand our emphasis on safety to an emphasis on health and safety. We need to change from being reactive to proactive. And we need to change the old attitude that safety is the concern of the Safety staff to an attitude that safety is everybody's business.

To do this, we must change our thinking on how health and safety organizations provide service.

We can improve our health and safety program. And we can do it:

- Without sacrificing quality;
- Without sacrificing our vigorous pursuit of new technology;
- And without sacrificing our competitive edge.

We can do this by integrating health and safety into the development of new technology.

A review of what's happening in the aerospace industry today shows a heavy emphasis on the development and exploitation of new technologies. Success in our industry is tightly linked to providing products that meet customer needs through application of state-of-the-art technology.

Other nations have learned from us that a superior technological capability is the key to national economic growth. They have mounted a broad challenge to our technological leadership, investing heavily in upgrading their own technologies and the capabilities of their products. The aerospace products of foreign competitors now equal or exceed ours in several important fields. For example, the long-held American superiority in civil aircraft is being severely challenged by foreign competition. This is exemplified by Airbus commercial jet transports, a number of advanced turbine engines, and commuter aircraft.

In response to this, the Aerospace Industries Association has identified eight technologies that are key to maintaining our market position.

- Very large-scale integrated circuits. This is considered a giant step in electronics. These circuits will provide computer systems with much greater computational capability, yet they will be smaller, lighter and easier to maintain.

- Software Development. This will demand large-scale improvement because computer systems are already generating more data than can be processed. Advanced software, the language and logic of computer operation, is rapidly becoming the key to the automated world of the 21st century.

- Propulsion Systems. Within 20 years, propulsion advancements could allow production of fighter aircraft with sustained speed capability beyond mach 3, and subsonic transports consuming 30 percent less fuel.

- Advanced Sensors. In tomorrow's aerospace vehicles, sensors will have to detect and relay more and more flightpath information. Some weapons programs demand sensors that automatically detect and identify very distant threats. Advanced sensors are required to provide that capability.

- Optical Information Processing. In the 21st century, conventional electronic systems may not be able to handle aerospace information processing requirements. The use of optical devices to store and manipulate data offers a thousandfold improvement in information processing performance.

- Artificial Intelligence. This is a technology that mimics human intelligence in dealing with complicated data processing and problem solution. It offers big improvements in performance, reliability and life-cycle costs of both military and civil aerospace systems.

- Ultrareliable Electronics, which are the next generation of flight control systems. They will require a level of reliability that far surpasses today's capability. Getting there will demand advancements in many separate electronics technologies and a knowledge of how to blend the applications of these technologies to increase the reliability of complex systems.

- And, last, the new technology that we're here to discuss this week: Advanced Composite Materials.

These advanced composites are a family of materials of diverse and sometimes complicated components. They offer significant weight savings, as well as far greater strength in relation to weight, when compared to current metal alloys. They offer high temperature resistance. They reduce life-cycle costs by making aircraft more fuel efficient, lowering manufacturing and labor costs, and providing corrosion resistance.

Use of advanced composites has increased dramatically in aerospace structure during the last two decades

Advanced composites allow us to build high-performance products; to meet Federal requirements for reliability and safety; and to compete successfully in today's competitive market.

They are the emerging structural material of the next decade, and will increasingly replace conventional metallics as we strive to build a lighter airframe that is more durable, more maintainable, and more fire-retardant.

But how does this tie in to employee health and safety? How do we integrate health and safety into the development of new technology?

Well, typically, when a new material is under development, or under consideration for use, we ask some questions. We often ask:

- Does it have good performance characteristics?

- Does it have long-term durability?

- Do we have the engineering skills required to exploit this material?

- Are the manufacturing processes in place?

But there are several more questions we've got to ask. We've got to ask if it will harm the employee or the environment. And we've got to ask if it will be accepted by the people who have to work with it.

Health and safety is a concern with new materials. We need to address health and safety issues early in the product development processes.

Development of new products is a complex lengthy process. It is the result of many separate processes that were often performed in a sequential manner. Information flowed between processes, but this information was often limited only to what was needed to perform the next process.

These processes were generally independent. Feedback could be characterized as focusing on correcting errors.

Unfortunately, errors often did not become apparent until the product hit the manufacturing floor or was in the testing process.

We have a new way of doing things now. Through continuous quality improvement, we've learned that product development should be a parallel, not sequential, process. A free interchange of ideas must occur during customer specification, during research, during design, and during manufacture and test. Today, we have made significant improvements. And the key has been the application of the concepts of Continuous Quality Improvement. We are working to continuously improve the quality of our products and processes and to understand who the customers are in this complex process and to satisfy their needs. This improved process requires the full participation of everyone involved in a two-way exchange of information and ideas.

As you can see, the process keeps improving. We've added one more component -- health and safety. It is absolutely essential that we integrate health and safety early during the product development cycle.

When Materials Technology specifies a materials, or when engineering develops a manufacturing process, they need to know the implications of the material in the workplace. New questions need to be addressed, such as:

- Is the material hazardous?
- Does it cause irritation?
- Does it have an odor?

- How should the tool be configured to allow the employee to perform his or her job safely, comfortably, and efficiently?
- Will protective equipment or local exhaust ventilation be required?

These questions bec.me drivers in the design of a safe, efficient workplace.

In order to answer these questions we have to rely on the expertise of the health and safety staff, not the staff of yesterday where we had only safety expertise, maybe not even the staff of today in which we've added an industrial hygienist. We'll have to rely on tomorrow's health and safety staff -- one that is composed of not only the safety and hygiene experts, but one that also has experts who can make a value-added contribution to the product development and workplace design process. We need these experts in toxicology, epidemiology, and occupational medicine

This range of expertise is essential because we cannot afford to stop and find a different material after we've committed ourselves to design. We cannot afford to backtrack It's too late to learn that there's an employee health concern after we're out there building the hardware. We know it takes time to get it right in the beginning. But getting it right in the beginning pays off in the end. Addressing the health and safety issues during the development process will allow us to improve the work environment and to reduce flow time and costs.

These actions I've been talking about will shape the aerospace industry's future. But what challenges does that future hold for us? Well, to properly answer that question, we need to have another conference. As I mentioned earlier, there are many challenges

But clearly, global competitive pressures will continue to increase, and trends in material technology will continue emphasis on the development and use of advanced composites. If we don't improve the processes for introducing new materials into the workforce, we can anticipate:

- Increased employee concerns about the work environment,
- Increased health and safety regulations, and
- Increased liability and costs.

If we don't listen to our employees, if we don't fully involve them in the development of a safe work environment that protects their health, and if we don't practice continuous quality improvement, we can end up with a work environment that employees fear working in.

We must view the workplace through the eyes of our employees; we must give them understandable and easily available information about the hazards of the work environment; and we must design the work environment with employee comfort, health and safety in mind.

Our challenge, then, is to build a forum that allows us to be proactive. We've got to actively influence legislation. We need to cooperate to establish permissible exposure limits for new materials. We need to cooperate in sponsoring and conducting research. We need to increase the professional expertise of our health and safety staffs. And we need to integrate health and safety into the way we work, getting everyone involved, from the beginning -- so that when we develop new materials, new processes and new products, we can ensure a safe and healthful work environment for all of our employees.

We can take an active role in influencing legislation. An example of that is the hazard communication regulation. We were instrumental in the development of that law. In order to adequately protect their employees, aircraft manufacturers needed information on chemical products they were using. "Hazard Communication" was a giant step in that direction. We know it's not a perfect regulation -- the information needs to be made more understandable to the employee -- but we can improve on that -- and we can use the quality improvement process to make it happen.

We can also lead the way in sponsoring research on the health aspects of new materials. But this must be a cooperative effort. If we're going to cut out non-value-added effort -- if we are going to stay competitive -- we can't afford to have the customer, the manufacturer, and the material suppliers all conducting independent studies.

We need to work together to identify problems and to research the solutions. And we need to do this before these materials hit the factory floor.

We can lead the way in health and safety by recognizing the importance of developing a professional health and safety staff. These experts can provide better consulting to the designers and builders of our product -- those who have the ultimate responsibility for a safe and healthful work environment. The result will be a better health and safety program.

The message here is that we can have our cake and eat it too. By incorporating health and safety into the continuous quality improvement process, we will enhance our industry's ability to develop and exploit new technology, and we will play a role in helping American industry maintain its leadership in the global aerospace market.

This is not an individual effort. It's not up to just the manufacturer or just the supplier. We've got to cooperate -- customer, manufacturer and supplier -- we've got to step up to this challenge. I'm confident that we'll succeed, and that a quality work environment -- in addition to competitive and high quality products -- will be the result of our efforts.

Thank you.

CRITICALITY OF COMPOSITES

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Good afternoon. We are living in a world of virtually exponential change. A world where we can create quantum-leap technological advantages; however, our world is also a place where we must adjust to and manage the side-effects, long-term impact, and general aftermath of what we do and the changes we have made. Often, we have very little precedence. Too often we are caught by surprise. Very often, the references of the past are obsolete for today's problem-solving environment.

Since we are living during these exponential changes in technology, a greater human effort is required to regroup and think about what we have done, sort out the short- and long-term effects, reprioritize our objectives, re-examine the known problems and project unforeseen possibilities, and put some collective effort on developing solutions. More often today than in the past, we do a lot of this concurrently.

My task in this important conference concerning advanced composite materials technologies is to describe the criticality of composites to the national defense Considering the changes in strategic military planning, the restructuring of United States' industry, the increases in international interdependence, the advances in multiples of technologies, and the differences in the industrial materials needed to manufacture modern military hardware, we need to cast the term "criticality" in a perspective that has some utility for us.

I'm going to illustrate the criticality of composites to defense historically, comparatively, militarily, and technically. I believe you will see, as I believe, that composite materials are here to stay with us for a number of reasons. The most important reason is the performance improvement they afford to a great many weapon systems.

First, let's look at a brief historical perspective. During World War II, the United States produced 310,000 military aircraft; 88,000 tanks; and a great number of other types of military hardware. These awesome numbers of military products manufactured were mass produced from an enormous industrial base that existed forty years ago. Many changes have occurred

since the 1940's as the United States gradually shifted from a mass production society to a services economy which employed upwards of 70 percent of its population.

The message is simple. We no longer have in place the industrial capacity to mass produce military hardware in those numbers. Further, we are no longer concerned with mass production as the number one national priority.

The breadth of United States' industry was also different forty years ago. We produced 56 different types of military aircraft during World War II using 19 prime contractors. Today, we have production runs for seven types of military aircraft using six prime contractors. However, the aircraft today are far more complex and far more lethal. The infrastructure is also complicated. Now, just for one aircraft type, as many as 2,500 suppliers in a vast matrix of sources supply the parts and components needed to manufacture the final aircraft Much of the supplies are obtained through catalogues. Many of these are foreign sources.

To press the mass production issue, there were 9,117 military aircraft produced by the United States in March 1944. This was the same month the Allies sent 1,600 aircraft to conduct the first bombing of Berlin. They were met by about 600 German fighters, and the rest is pretty well known. My point here is that the United States no longer has such military missions envisioned in our national strategy, nor do we require such immense production capabilities to support such numbers. The situation is worse in merchant ship construction. The maritime situation is not our case for discussion today. But, it helps illustrate the industrial demise of domestic industry in some areas that were dominant forty years ago.

The two leading tactical aircraft technologies under full production in World War II and today are well represented by the P-51 Mustang and the F-15 Eagle, respectively. The P-51 was developed as a fast, long-range fighter and participated in escorting the bombers over Berlin in March 1944. But, in comparison with the F-15, we now fly at mach speeds rather than miles-per-hour, we power aircraft with gas turbines instead of reciprocating engines; we carry tactical missiles rather than machine guns; and we fire weapons with sophisticated electronics instead of iron sights. Times have changed. But, it is also surprising how many people still think in terms of mass missions, mass production and, of course, metal aircraft.

Remember the vast armadas flying in bomber formations over industrial targets to drop iron bombs? Bombardiers took celestial navigational fixes through a little bubble at the top of the bomber and guided the final approach over the target using the famous Norden

bombsight or some variation. In contrast with the B-1, the missions, payload, avionics, and countermeasures are quite different, extremely complex, and very expensive. The newer models are even more complicated, and some do not even have the same appearance as these.

Our bombers, or launch platforms, don't have to be able to fly over the target in every case. We can launch cruise missiles hundreds of miles from our ultimate target. We reduce risk to the aircraft and crew, returning the launch platform safely for another load of cruise missiles. Ground-to-air or ship-to-air missiles reverse the technology threat in true military countervailing fashion. Missions have changed. Weapon systems have changed. Threat environments have changed. The United States' industrial structure has changed. The technology base has changed.

To capitalize on our brush through aerospace weapon technologies, helicopters have, in fact, revolutionized land warfare forever. Vietnam and Afghanistan have, without doubt, provided universal acknowledgement of the helicopter's adaptability to land warfare. From the fixed-wing perspective, the AV-8B Marine Corps jump jet, our version of the British Harrier, can support ground forces from aircraft carriers, airfields, austere land sites, and amphibious shipping since the AV-8B is capable of vertical and short take offs and landings Each of these illustrated is with significant technological progress. Each case illustrates reliance on engineering and structural improvements to achieve its intended mission performance. The decision process to design and produce such capable aircraft to meet specified mission needs begins early in the weapon system planning process.

From a materials engineering point of view, our objective is rather simple. Look at the expected threat environment, postulate which capabilities are needed to provide superiority during some measured point in time, design the hardware for production during that time frame, then produce the systems and equipment and support needed to meet the mission The traditional objectives don't change very much. But the solutions have become based on technological options which are more complicated with an emphasis on new materials without which the objectives cannot be met.

Only seven years ago, the President sent his National Materials and Minerals Program Plan and Report to Congress. In that report, the President identified national defense needs for traditional or common industrial materials. The report stated that there was a new

dimension in advanced materials utility being emphasized by the Department of Defense The most significant emphasis at that time was composite materials.

Industrial materials are the basic elements from which we construct commercial and military products of various forms and shapes. We can identify essential uses of some materials from a matrix that illustrates which key materials are used pervasively in military hardware and without which the United States would be unacceptably dependent on foreign sources during national emergencies. We have been aware of the traditional materials, such as chromium, manganese and others, used for making steel since long before World War I.

Strategic and critical materials led the way for many of the military, industrial and social changes of the past. Historians have named periods after materials, such as the Bronze Age, the Iron Age and the Industrial Revolution which is associated with machinery and the production of steel. In fact, manufacturing progress is directly attributed to new and revolutionary uses of metals, whether one relates metal to more efficient capital equipment or to higher performance in final products. Now we are moving on to advanced composites, ceramics and powder metallurgy.

Look at the paralleled military perspective. Steel paved the way for improved ships over wooden hulls and also provided the armor needed by tanks to overcome the trench warfare tactics installed during World War I. Aluminum made possible the high performance aircraft of World War II. Cobalt provided the higher temperatures needed by gas turbine engines, and titanium gave us the airframes needed to produce the jet fighters of the Korean and Vietnam eras. Depleted uranium gives us new armor penetrators used in A-10 ammunition, and composites provide the improved spacecraft designs. It goes on and on.

My point is that we in the Department of Defense are always looking for ways to extend range, reduce fuel consumption, and increase payload carrying capability And, I should add, there are no new weapon systems that do not have new materials in some form to meet their mission requirements on the battlefield.

Now, let's look at the use of composites in some modern weapon systems and why composites are going to be around for a long time. The largest use of composites in military hardware is our use of carbon fiber to make organic composites. The Marine Corps AV-8B provides us with a baseline for some of the illustrative remarks needed The AV-8B materials distribution chart shows how carbon fiber composites are used in the aircraft as compared to the other more traditional materials, such as aluminum (see Fig. 1) The AV-8B is the

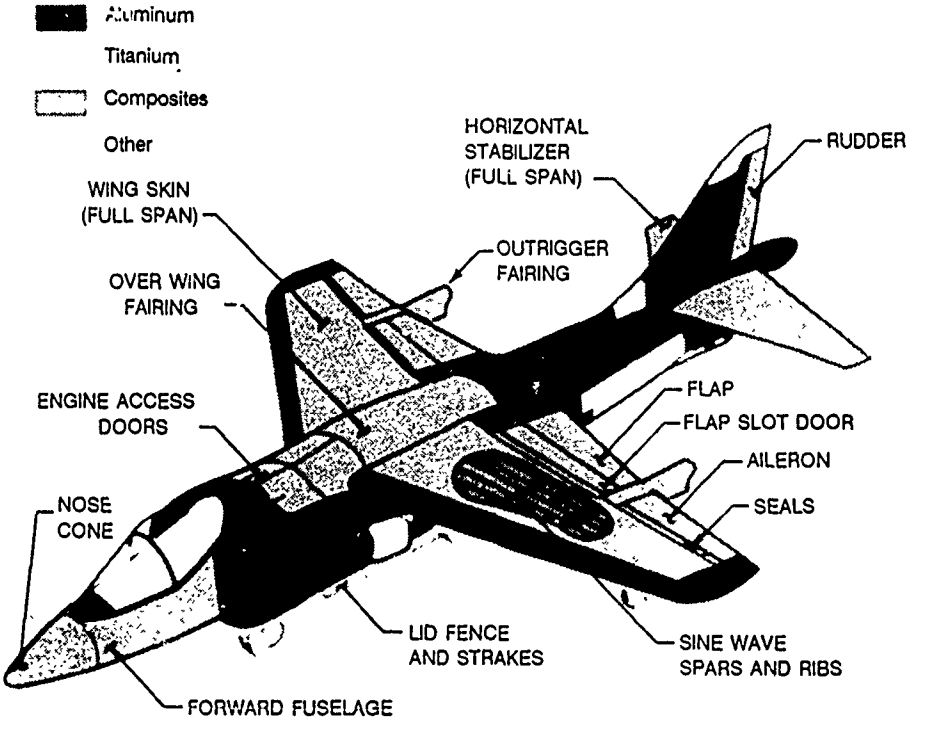

Figure 1. AV-8B composite applications.

United States version of the British Harrier jump jet which performed so well in the Falklands a few years ago. However, the AV-8B can carry double the payload of the Harrier due to the improvements shown with composite applications. Doubling the payload carrying capability is not a marginal improvement; doubling any performance capability is very significant in terms of product worth and dependability.

The use of composite material structures in tactical aircraft and helicopters is an evolutionary trend, not revolutionary. Early trials and substitutions occurred in the 1960's, and, as confidence in the new materials increased, more of the new composite materials were included in follow-on production models resulting in large amounts of structural weight savings. Soon, hardware designs started to be based around the material rather than relying on the substitution approach alone. Now, the new designs for advanced aircraft cannot be returned to metal since performance depends on composite materials.

Tests have shown that certain composite materials are actually stronger than metal when used properly. For this reason, an aircraft can be designed and constructed with a forward swept wing, such as the X-29. Said another way, the aircraft with the forward swept wing cannot be produced to achieve the performance required without composite materials. Comparative test results are conclusive and clear.

From the evolutionary perspective, use of advanced composite materials structures has increased to the point that every foreseeable generation of strategic and tactical missile, strategic and tactical aircraft, and certain spacecraft will use composite materials in some form. The dominant form of composite material being used is based on carbon fiber. The prevailing precursor for carbon fiber is polyacrylonitrile, or PAN-based carbon fiber.

The last Department of Defense calculation of military needs for PAN-based carbon fiber indicated that we would increase defense consumption of PAN by a factor of five in ten years. Consumption take off occurs this year according to our estimates. All this demand is based on measured production commitments for a number of military systems. Therefore, our estimate may be conservative.

Department of Defense materials and structures priorities have three mission areas: space, missiles, and aircraft. To meet these missions, there are three technology areas: composites, rapid solidification, and laser hardening. From this foundation, we develop a science and technology program.

If we break out the mission, priorities, and technology needs further, we can see the material thrusts with which we can be more specific in our intended applications. With data such as this, you can now see a little better into the future. You can see where we are heading (see Fig. 2). Please note the thrust column which indicates the pervasive use of various composite materials for military purposes. You may ask: How universal or how isolated is the United States in its use of composite materials? The answer adds another dimension to our discussion.

Commitments to the use of composite materials by foreign countries have been very significant. The following countries using composite materials are the United Kingdom, West Germany, Italy, the Netherlands, Spain, and Sweden. France is very advanced in the use of composite structures. Japan is moving very swiftly in composites technology. As you can see, composites are an international phenomena with sound implications for increasing use.

Even though the United States is the primary consumer of composite materials at this time, from an international market perspective, we are not simply the world leader based only on consumption by quantity. We have much to do to even stay in international competition with the technology.

Yet, there is another important reason for specific consideration of just how essential composites are to defense.

Reflecting on all these various perspectives we have used to discuss composite materials, we have looked at composites with a rather earthy viewpoint. Space, however, provides us with a unique medium through which to examine composites technology just a little further. We do not have hundreds of years of experience in space. Thus, we have no enduring bias, or tradition, to overcome. Since space warfare has never been waged, it has no historical relevance. Space is almost completely forward looking. Space can help us reach forward because there are no atmospheric boundaries. And, space has great relevance to the technological progress of composite materials.

The Strategic Defense Initiative Organization has been described as an aggregation of space research and development projects. Perhaps, we can view space as a new and different military mission. For example, once deployed, space systems function without logistics support. So, we must design for longevity and survivability in an isolated environment. Spacecraft are essential to all military operations, and they are vulnerable. There is no place to hide in space.

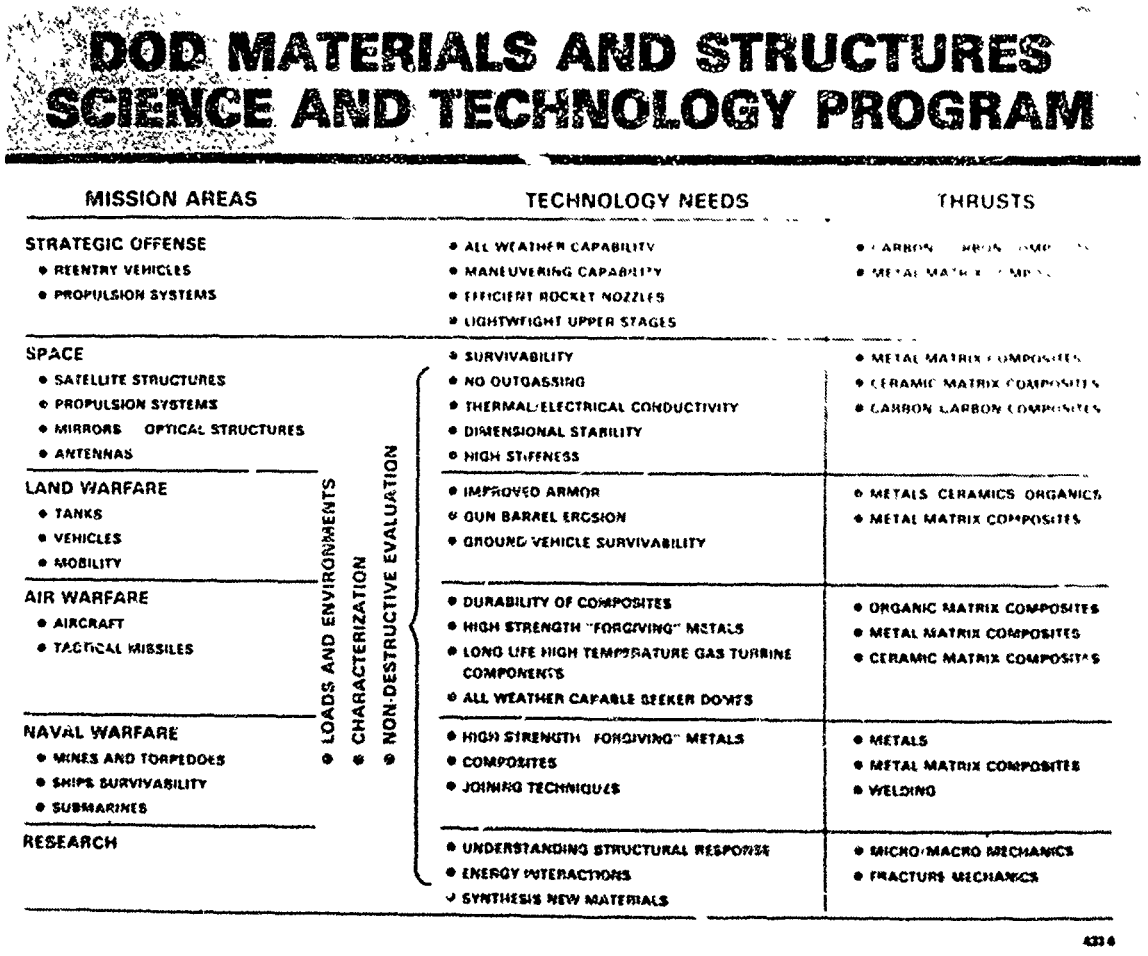

Figure 2. DoD materials structures and technology program.

The threat environment in space is unique. Space is not atmospheric, and space is open territory. So, we must develop a series of survivability approaches to potential threats for which there is no established precedence. In this case, our experience in past wars has even less to offer as a baseline for problem-solving, either from a military or a technical point of reference.

Our approaches to this kind of problem solving are, however, very technical in scope and application. Each approach has weight implications. Not weight in space; weight for the lift-off equation. So, a matrix of solutions with techniques and implications are developed. This is a slightly oversimplified version to illustrate the complexities involved (see Fig. 3). You can see, however, that the structural materials will be primarily composite materials in some form (see Fig. 4). We can say, therefore, that space technology is integrally linked with composites technology.

Returning to atmospheric boundaries, we can also say that carbon fiber composites, sometimes called organic composites, are not the ultimate in materials technological design. Some predict that organic composites will be subjected to competitive development of advanced metallic technologies over the next decade or two. Perhaps, that will be true. Meanwhile, we have a lot of work to do to deal with the phenomena of carbon fiber in the here and now. Each of us, both organizationally and individually, may have our own views and efforts on the impact of carbon fiber in our own area of expertise and responsibility. And, there is enough career load there for a lot of people.

At this time, more than $80 billion in committed military hardware production will use composite materials in some form. The $80 billion has been a fairly stable estimate for a few years. I can qualify it to say it is a deliberate overstatement and is the value of the purchased weapon systems to use composites and not the value of the composites. But, the statement does illustrate the pervasive use of composites in a very wide variety of weapon systems to be purchased.

The challenges to the United States manufacturing base are greater today than at any time in history due to the international focus on the entire set of circumstances. It makes our jobs just that much more difficult.

SPACECRAFT SURVIVABILITY APPROACHES (SURVIVABILITY ≈ WEIGHT SAVINGS)

SURVIVABILITY	TECHNIQUES	WEIGHT IMPLICATIONS
AVOIDANCE	MANEUVERING ORBIT VARIATION AUTONOMY	ADDITIONAL FUEL, TANKAGE, PROPULSION SYSTEM REQUIREMENT AUTONOMY SENSORS AND CONTROLS
DECEPTION	DECOYS CHAFF AEROSOLS SIGNATURE REDUCTION	DECOY AND DISPENSING SYSTEM WT (BALLOON DECOYS ~5 LBS EACH) CHAFF/AEROSOL AND DISPENSING SYSTEM WT (CHAFF SYSTEM 10-15 LBS RADAR ASSORBING MATERIALS WEIGHT
HARDENING	LASER NUCLEAR BALLISTIC SHIELDS	SHIELD AND ATTACHMENT WEIGHT PENALTY
REDUNDANCY	SILENT SPARES REPLACEMENT LARGE CONSTELLATIONS	ADDITIONAL LAUNCH VEHICLE WEIGHT VOLUME REQUIREMENTS
SELF-DEFENSE	SHOOT BACK THREAT LAUNCH INTERDICTION	ON-BOARD DEFENSE SYSTEM WEIGHT (WEAPON, CONTROLS, FUEL)
INTRINSICALLY HARD MATERIALS	HIGH TEMPERATURE STRUCTURAL INTEGRITY HEAT DISSIPATION CAPABILITY NO INDUCED OUTGASSING CONTROLLABLE SURFACE PROPERTIES	NONE FOR ADVANCE LIGHT WEIGHT METAL MATRIX COMPOSITES

Figure 3 Spacecraft survivability approaches (survivability ≈ weight savings)

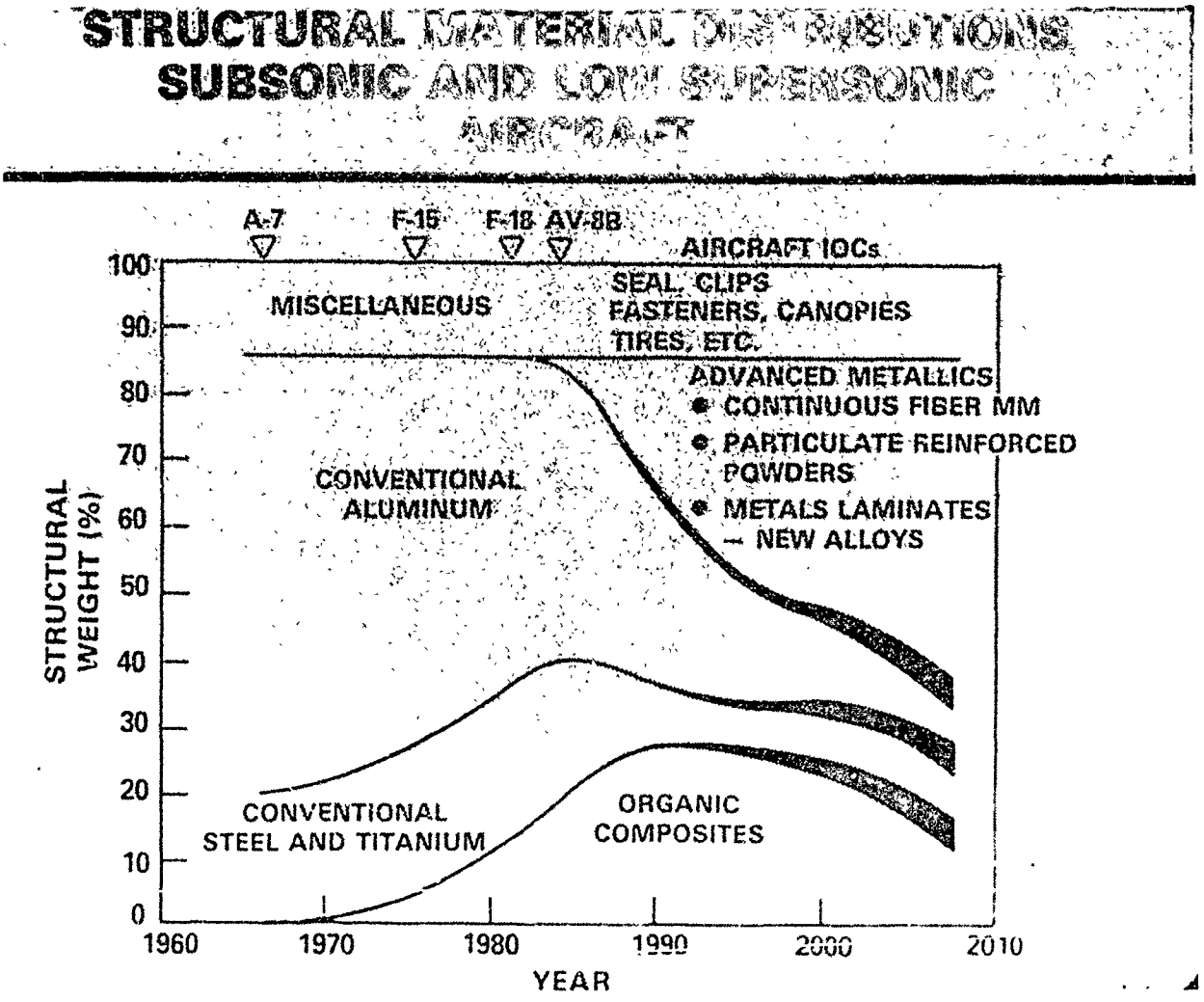

Figure 4 Structural material distributions - subsonic and low supersonic aircraft

Fundamentally, the Department of Defense objective is to provide the military forces with the best hardware we can develop, manufacture, and deploy. We must also maintain sufficient production of military hardware during both peacetime and national emergencies. At this point in history, that second objective is becoming increasingly difficult to achieve.

In closing, it is my intention that our discussion of the criticality of composites covers a broad range of the topic and that it is helpful in meeting your own responsibilities. We are witnessing an increasing rate of technological change during this historical time frame. That calls for some pretty intensive data exchange so we can all do our jobs properly.

III. COMPOSITE TECHNOLOGY OVERVIEW

CONSENSUS STATEMENT

This session reviewed advanced organic polymer matrix resins and continuous high strength, high stiffness fibers to develop a common understanding of advanced composites. Areas addressed were applications, materials manufacturing and use of composite parts in aircraft manufacturing, supportability, and future advanced composite materials.

Polymer matrix composites are materials made from two distinct phases - an organic polymer resin binder or matrix and a continuous fiber used as reinforcement to achieve properties not otherwise attainable. The strength and stiffness characteristics are equivalent or superior to aluminum, the metal with the highest strength to weight ratio. There are a number of resin systems used today in combination with such fibers as boron, glass, aramid, and carbon or graphite.

The use of composite materials over time has increased dramatically. The percentage of airframe structural weight made of composites for military aircraft has risen from the 3-5 percent level for F-14, F-15, and F-16 aircraft in the late 60's and 70's, to 27 percent for the AV-8B, with projections of 40-60 percent for emerging aircraft such as ATF and ATA. The usage of composites at one aircraft manufacturer alone is expected to increase during the next decade from the current level of about 100,000 pounds to over 1,000,000 pounds annually.

Polymer matrix resins and their prepregs are chemically reactive systems by design. The unreacted materials present a variety of potential hazards to those who work with them. The degree and the scope of the hazard depend significantly on the particular resin system and how it is handled. There is a diversity of forms, processes, and raw materials. How materials are combined and how materials are normally handled in the workplace were reviewed. There are various polymer matrix resin systems that are currently based on epoxy compounds, polyesters, phenolics, silicones, and polyimides such as bismaleimides (BMIs).

Part forming processes also are numerous and range from high worker-contact hand layup to automated tape-laying machines that reduce worker contact with reactive resins. Although many automated or semi-automated forming processes (such as filament winding, machine tape laying, braiding, and pultrusion) are available, hand-lay operations are still quite

common in the industry. The F-16 was used as an example to illustrate several applications of the three main steps in manufacturing using composites, and the interaction of the human element in each step. Layup (the placement of composite material onto the part mold) was demonstrated by showing the fabrication of stabilizer skins and fiber glass covers. Processing or curing (the application of heat and pressure to consolidate the laminate and cross-link the matrix) was illustrated with autoclave, press, and oven operations. Machining (drilling, trimming, and routing of the processed laminate) was demonstrated by showing the assembly of stabilizer skins.

With extensive expansion of applications and usage, worker exposure to composite materials will increase at all levels of operations, even with current automated processes. Exposures will occur in laboratories due to material sampling, inspection, and receiving testing. In the manufacturing shop, exposures will increase due to the larger sizes of composite parts, greater number of material rolls or containers, and increased number of parts to be handled and/or observed. Ultimately, new automated and non-automated robotic processes will be necessary, not only for increased productivity and cost savings, but also for the health safety of the worker by minimizing exposure.

Supportability of advanced composite structures was addressed using examples from McClellan AFB. Supportability is a tremendously broad subject. It includes everything from the basic design concept of the structure, to how that particular structure meshes with other structures in the weapon system. Supportability also involves the specific materials used in manufacture, technical data, repair methods, training, and the personnel and support equipment required to keep that structure functional.

The future offers many unique opportunities for the development of higher performance composites. Epoxies, including new phase toughened resins, will be most widely used; but polyimides and BMI's will continue to increase their percentage of the market. Thermoplastic resins will continue to grow in usage as improved manufacturing methods and better materials evolve. As part of the Air Force's Project Forecast II, new technology efforts are being pursued to support the development of ultra-lightweight composite aircraft that are 50 percent lighter than current high performance aircraft. This will require a combination of new materials technologies, with the principal focus being on higher performance reinforcing fibers. Ordered polymer and molecular composite technologies will also be pursued.

QUESTIONS ASKED

Although waste disposal of composite materials is not perceived as a problem, it was felt by several individuals that this area needs to be examined further. If this is a problem, a subset of this issue is how to handle the disposal of hazardous materials which may also require demilitarization prior to disposal. Training questions asked were threefold:

1) How does the Air Force train its people to do composite repair and maintenance?

2) What worker safety training programs are in place at manufacturing plants (chemical producers, composite suppliers and users)?

3) Should training on safe handling and protection be part of the MSDS?

This last question is tied to the need for information regarding the chemicals used. It is a challenge trying to balance the safety needs of the customers and their employees with the need for security to protect proprietary materials.

OVERVIEW OF TECHNOLOGY OF ADVANCED COMPOSITES

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Environmental Resource Management

Lee McKague, Chief
Composites, Materials and Processes

B. G. W. Yee, PhD, Manager
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ABSTRACT

Many trade journals and industry news services have long been predicting and reporting an exponential growth in the application and use of composite materials. This has been graphically reflected as percentage of airframe structural weight made of composites over time for military airplanes. This percentage has risen from the 3-5 percent level for F-14, F-15, and F-16 aircraft in the late 60's to 70's up to 30-50 percent for emerging aircraft such as ATF, ATA, and B-2.

The F-16 itself provides an example of this expanded usage. As originally designed in the mid 70's, only about 3 percent of the structure was made of advanced composites. These applications were to the skins of the empennage, where graphite-epoxy is used. Today, a new model of the F-16, the Agile Falcon F-16, is being planned for production in the 1990's; and it will have about 20 percent of its structure made of composites. In addition to empennage skins, wing skins, access doors, stiffeners, and other structural members will be made of composites.

As a result of these new applications and similar ones on all new aircraft programs, annual usage of composites at General Dynamics, Fort Worth (GD/FW) is expected to increase during the next decade from the current level of about 100,000 pounds to well over 1,000,000 pounds annually.

Many materials and material forms are involved in this expansion. Thermoset resins will continue to be widely used with graphite fibers. Epoxies, including new phase toughened resins, will be most widely used; but BMI's and polyimides will continue to increase their

percentage of the market. Thermoplastic resins will continue to grow in usage as improved manufacturing methods and better materials evolve, and as confidence increases in these materials.

Part forming processes also are numerous and range from high worker-contact hand layup to low worker-contact resin transfer molding. Although many automated or semi-automated forming processes are available - such as filament winding, machine tape laying, braiding, and pultrusion - hand-lay operations are becoming quite common in the industry.

With the significant planned expansion of application and usage, there is potential that worker exposure to composite materials could increase at all levels of operation, from the laboratory through the manufacturing shop. The challenge for the future is to provide the necessary procedures and orientation that will allow actual reduction and worker exposure even though usage of these materials is dramatically increasing.

INTRODUCTION

We view the new composite materials innovations being as revolutionary as early transitions from wood or metal tube structure covered with doped fabric, to wood/plywood fabrication followed by metal structure and skins. This new composite evolution provides for better strength to weight ratios, modulus and other designs enhancements. In addition, they are non-metallic, thus inherently corrosion noble.

That virtue will allow us to eliminate many hazardous waste generating processes for metals such as most degreasing, tri-acid deoxidizer and the Forest Products Laboratory (FPL) pre-bonding etchant for aluminum adhesive bonding. These latter two contain chromates that are environmental concerns. Our perception is that it may be possible to eliminate chromates from the prime paint coat currently required for metallic outer surfaces. In essence then, we may take advantages of composites' unique properties to eliminate many traditional hazardous wastes and chemicals of concern from our workplace.

On the other hand, composite materials also have constituents of concern that must be addressed at the onset of manufacturing with respect to environmental, health, and safety considerations. Recognizing these potential problems and implementing the proper controls

for protection of the workers and our earth's environment is part of the management challenge of more composites materials in aerospace manufacturing.

OVERVIEW

The composites application trend is growing exponentially as shown in Figure 1 for the chronology of 1960 into the early 1990's. This illustration also reveals the current in-service materials, near term, and future anticipated materials. Note that there was very little percent usage as late as 1970 with the early models of the F-16 containing only about 2.5 percent (Fig. 2) composites. As newer models of the F-16 emerged, composites technology continued to develop. We are now projecting about 20 percent composites for our latest design improvement, the Agile Falcon (Fig. 3). By the use of composites, new lightweight aluminum alloys, and other innovations, this aircraft will have remarkable performance and maneuverability. Details of these new designs and selected material are shown in Figure 4. Other details for skin and wing construction show baseline materials of aluminum, graphites/thermoplastics, graphite/bismaleimide (BMI), glass/BMI and honeycomb core (Fig. 5).

Perhaps you are aware that we have a variety of commitments from several sources for new aircraft. Some of these and the anticipated by weights of projected materials are shown in Figure 6. When we project this into future annual tons of use, we see rapid rises in tonnage in the early 1990's (Fig. 7).

With this increased variety of materials with different preferential forming methods, we will see many types of fibers, thermosets, and thermoforms innovated into material forms more amendable to their most optimum manufacturing process as illustrated in Figure 8. This will give rise to shape forming processes such as ply-on-ply buildup, mass build up, and mold forming (Fig. 9).

Similarly, thermoplastic manufacturing processes will consist of new operations such as ply stacking, preheating, press mold thermoforming, mating, and assembly consummated by thermoplastic welding (Fig. 10). This will lead to a high degree of involvement by typical

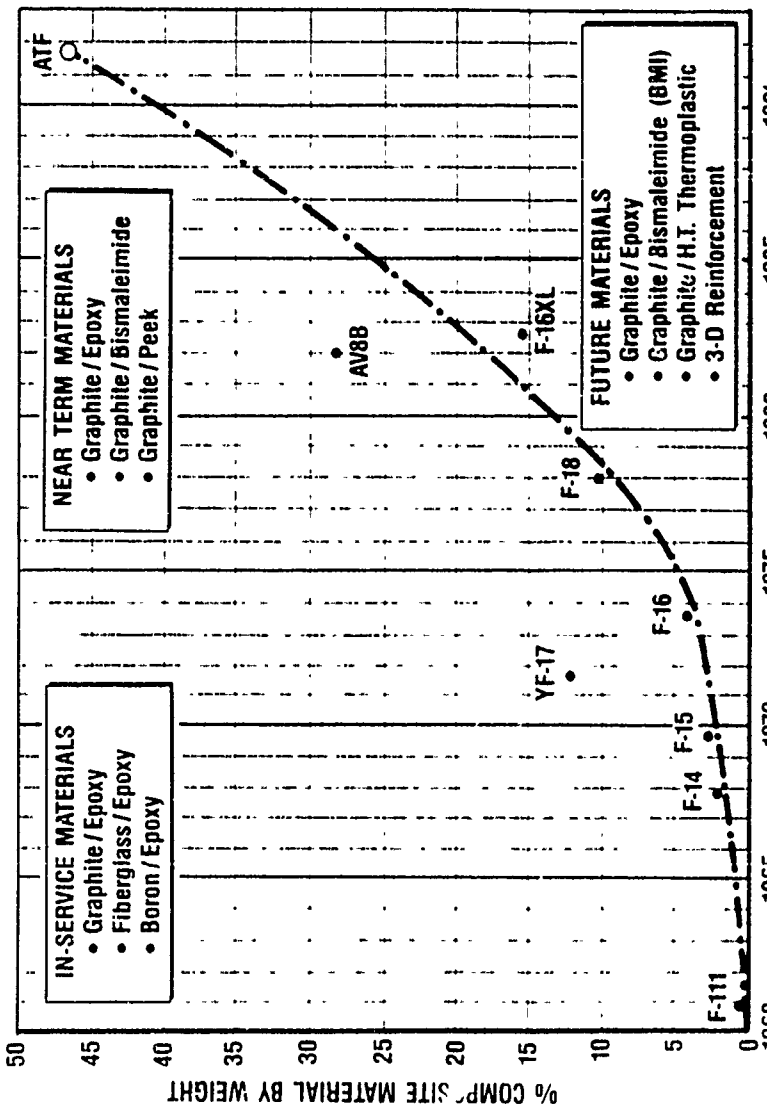
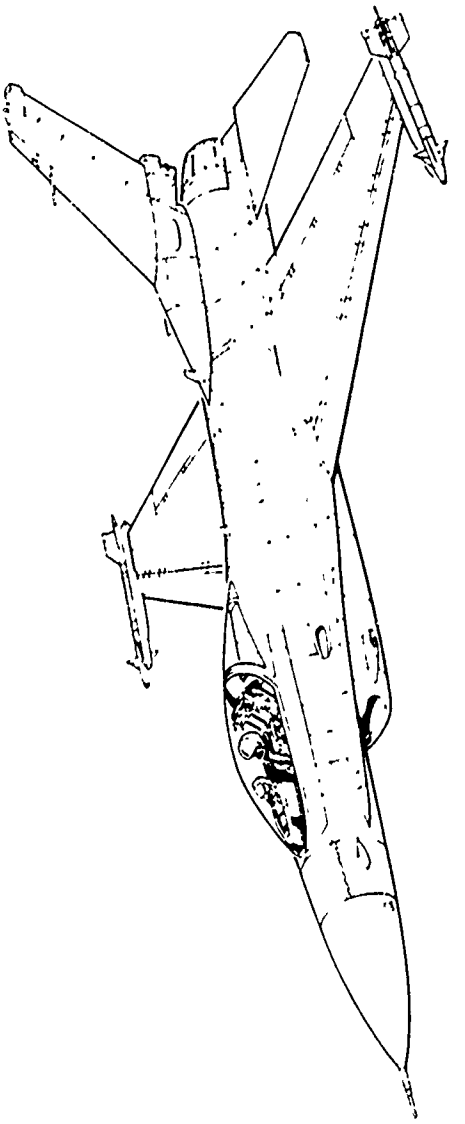
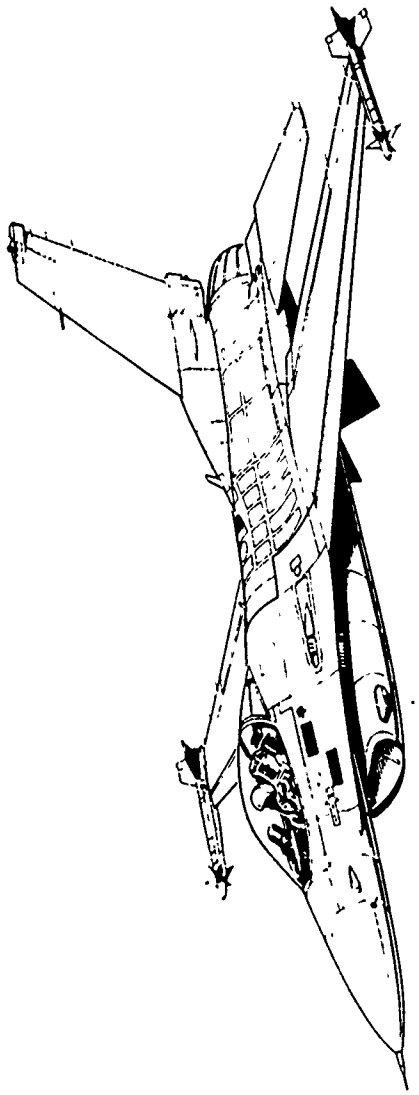


Figure 1 Composites applications are growing exponentially.



ACTUAL STRUCTURAL COMPOSITE WEIGHT: 240 LBS → 2.5%

Figure 2. The F-16C/D represents mid-70's conservation.



PROJECTED STRUCTURAL COMPOSITE WEIGHT: 2,000 LBS → 20%

Figure 3 Agile Falcon F-16 is an example of new composites usage.

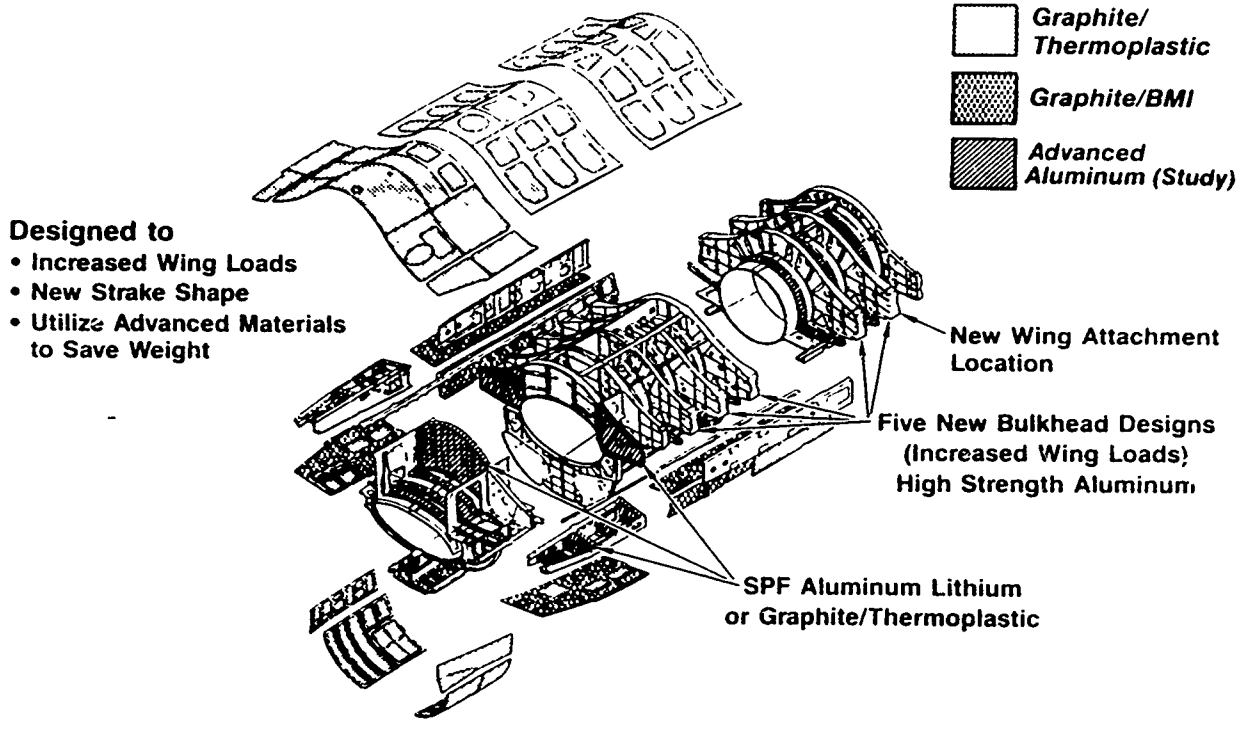


Figure 4. Center fuselage design involves advanced materials.

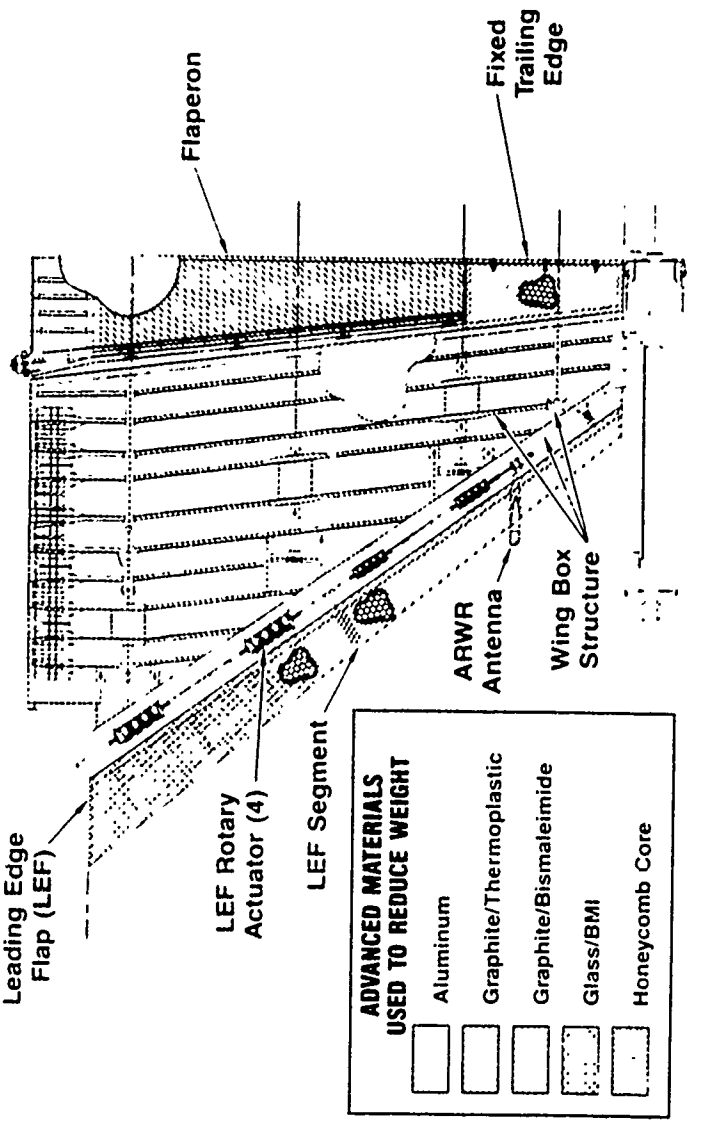


Figure 5 The wing will have composite skins and spars.

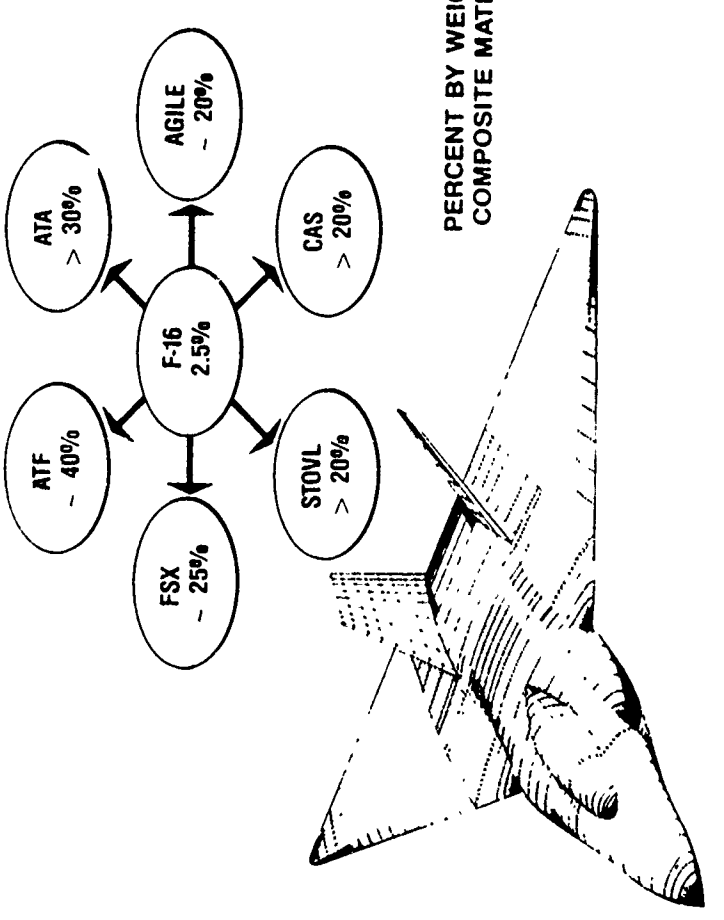


Figure 6. Many other programs involve extensive use of composites.

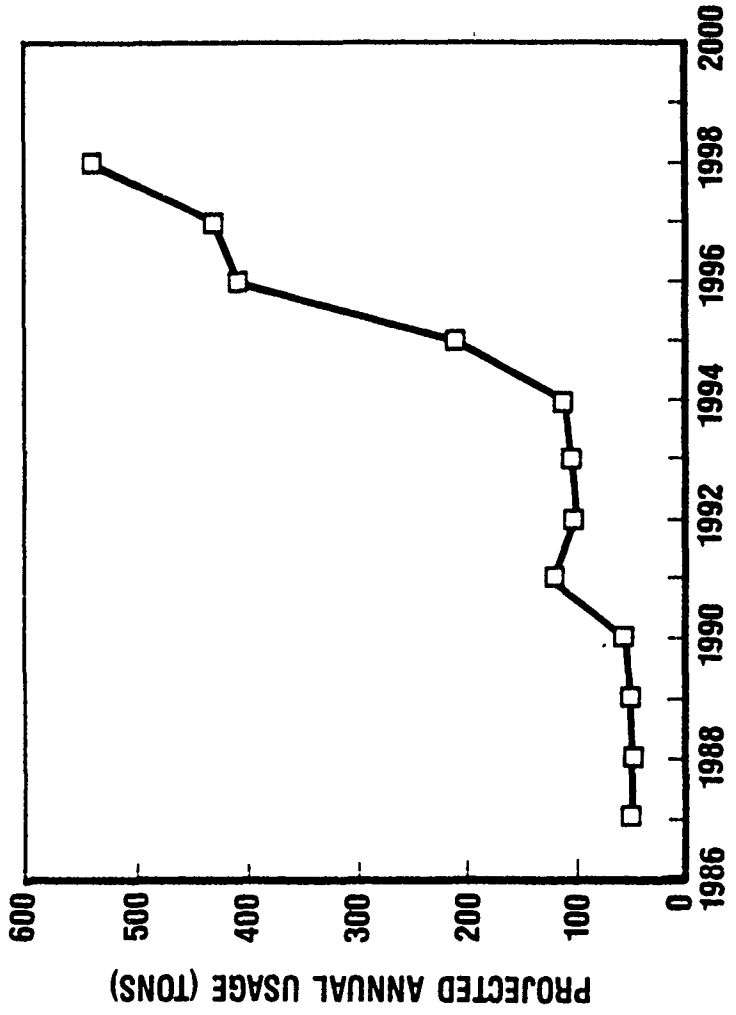


Figure 7. Annual usage of composites will increase dramatically at GD/FW.

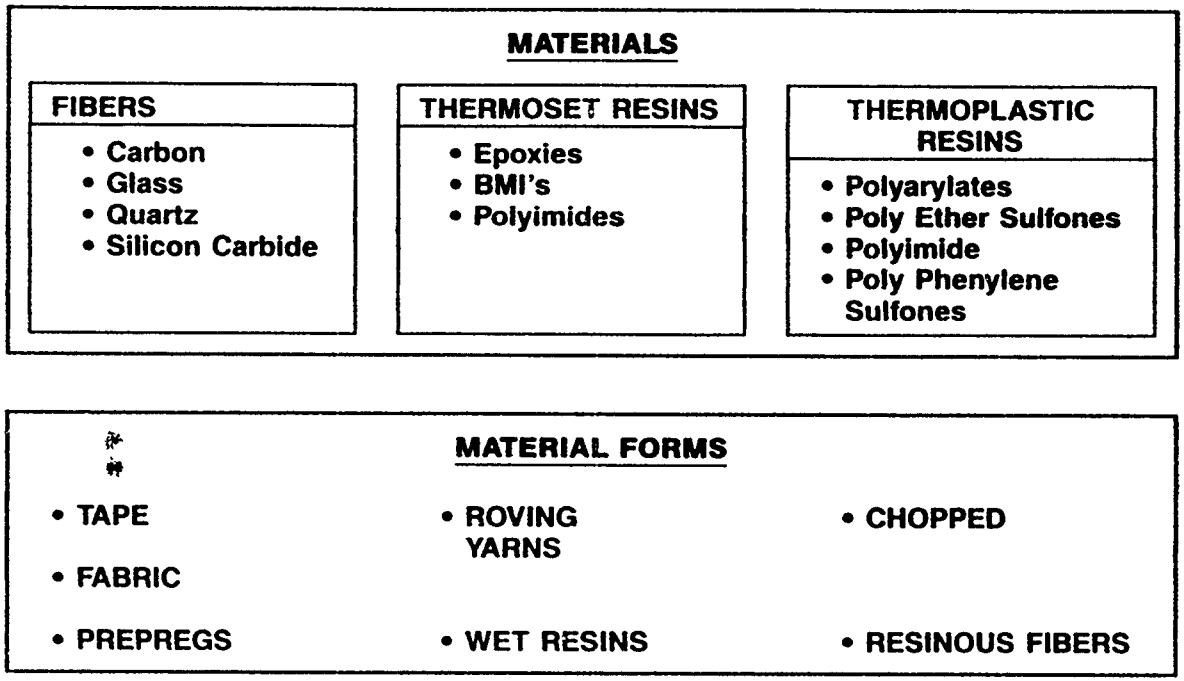


Figure 8. Many materials and material forms will be involved.

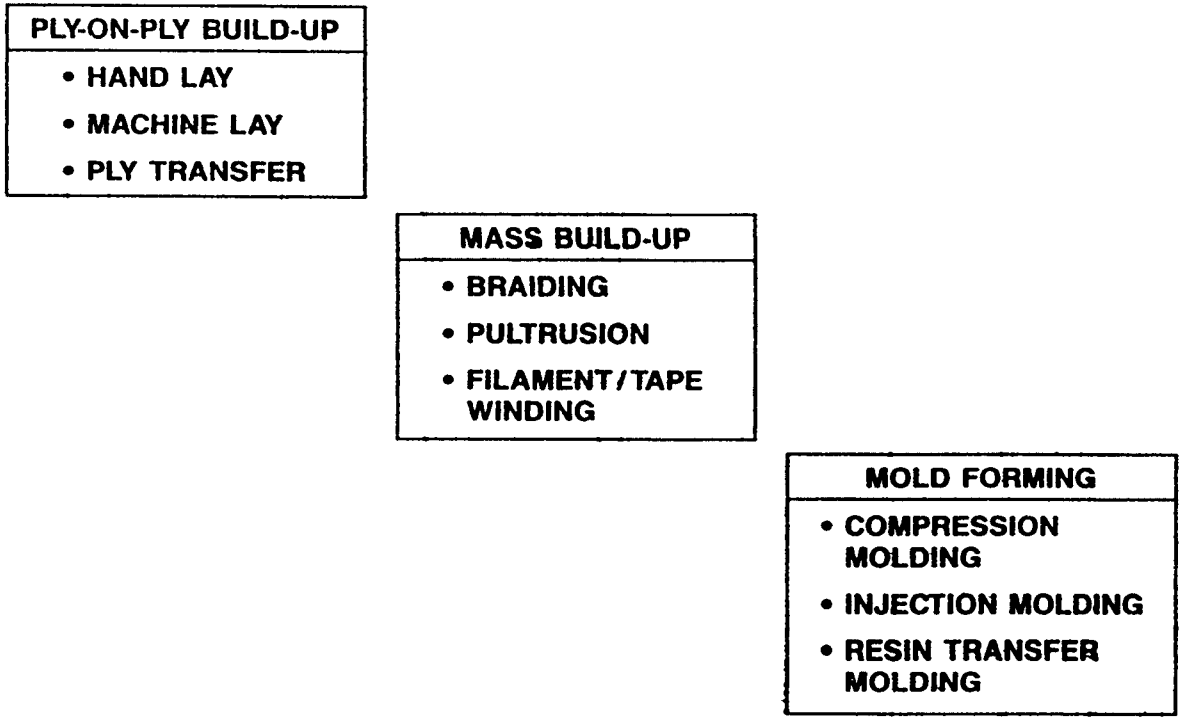


Figure 9. Part forming processes are numerous.

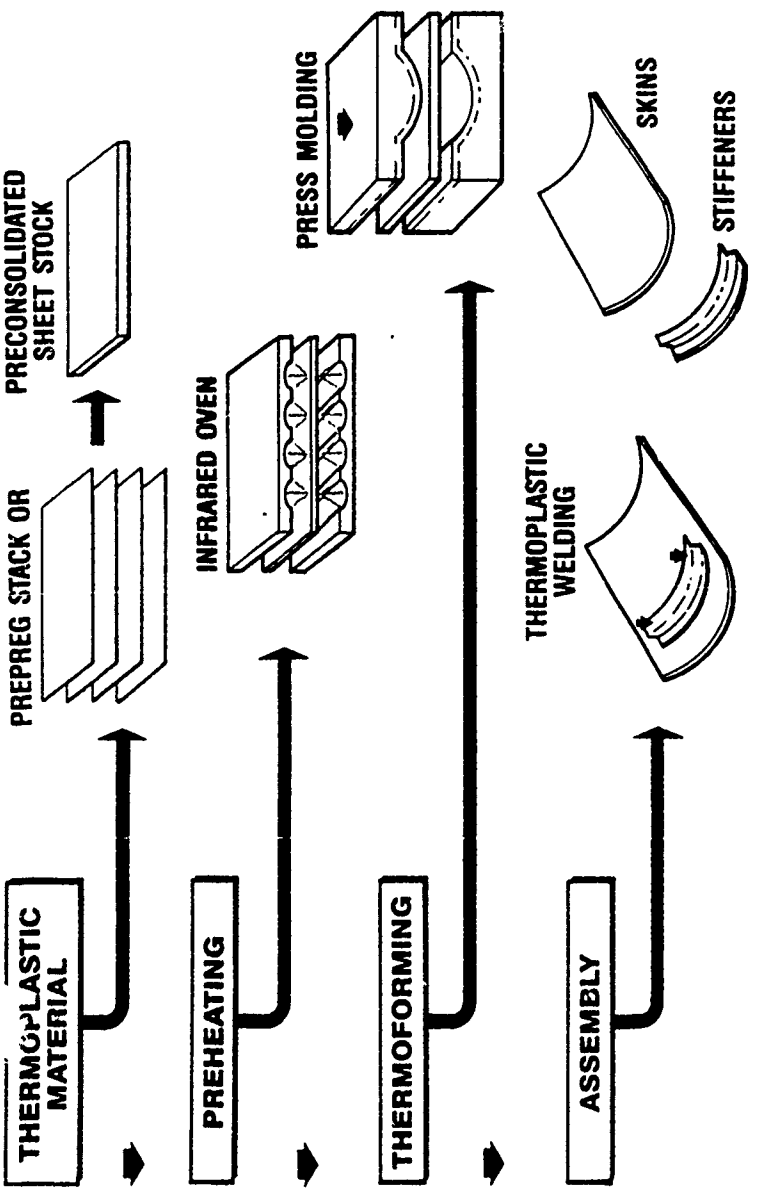


Figure 10. Thermoplastic processing involves new operations.

manufacturing operations of receiving inspection/acceptance testing, detail parts fabrication, and parts machining by various means as illustrated in Figure 11. Subsequently, they will proceed to components, sub-assembly, and final assembly culminating into the surface finished final product.

This attendant scale-up will invariably increase worker exposure to larger surfaces with increased emissions by a variety of manufacturing processes. From manufacturers' Materials Safety Data Sheets (MSDS) revelations on hazard materials percent composition and accompanying recommendations for proper worker protection such as ıoods, respirators, and protective clothing should be incorporated in the beginning. Their integration into first Research and Engineering Materials and Processes Laboratory properties testing should follow. This should provide the elements essential for scale-up.

The evolved Materials and Processes specifications, such as our GD/FW FPS's (Process Specifications) and FMS's (Material Specifications), should include all potential information on environmental, health, and safety materials. As the processes evolve through pilot scale and early prototype development, more appropriate and explicit procedures with inputs for occupational health specialists should be incorporated into specifications such as our GD/FW Process Specifications and others. This up front action by all concerned parties should negate the possible problems of dermatitis and exposure to hazardous materials above current acceptable exposure levels from scale-up shown in Figure 12.

We have had our own experiences when we fabricated two prototypes of the F16-XL delta wing stretch high performance model using V378A's BMI/Graphite wing skins (Fig. 13). Early in the laboratory investigations the effluents were determined to be divinyl benzene (DVB), ethyl vinyl benzene, and diethyl benzene. The major constituent DVB was shown to be less than 1 ppm in the assembly workplace (Fig. 14), and no health effects have emerged.

The lessons learned lead us to pay close attention to the MSDSs for accuracy and completeness, plus identify and monitor the effluents in early laboratory test specimens fabrication and testing and convey that information all the way to completely informed workers prior to their first stages of manufacturing (Fig. 15).

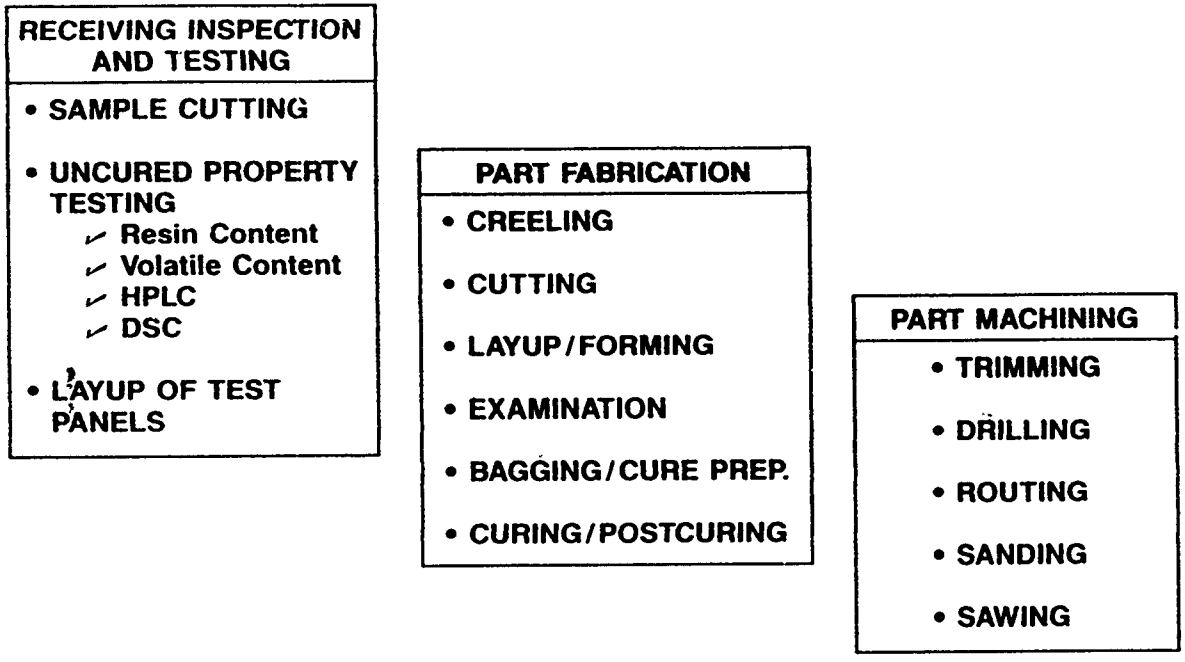


Figure 11. Users have a high degree of involvement with the materials.

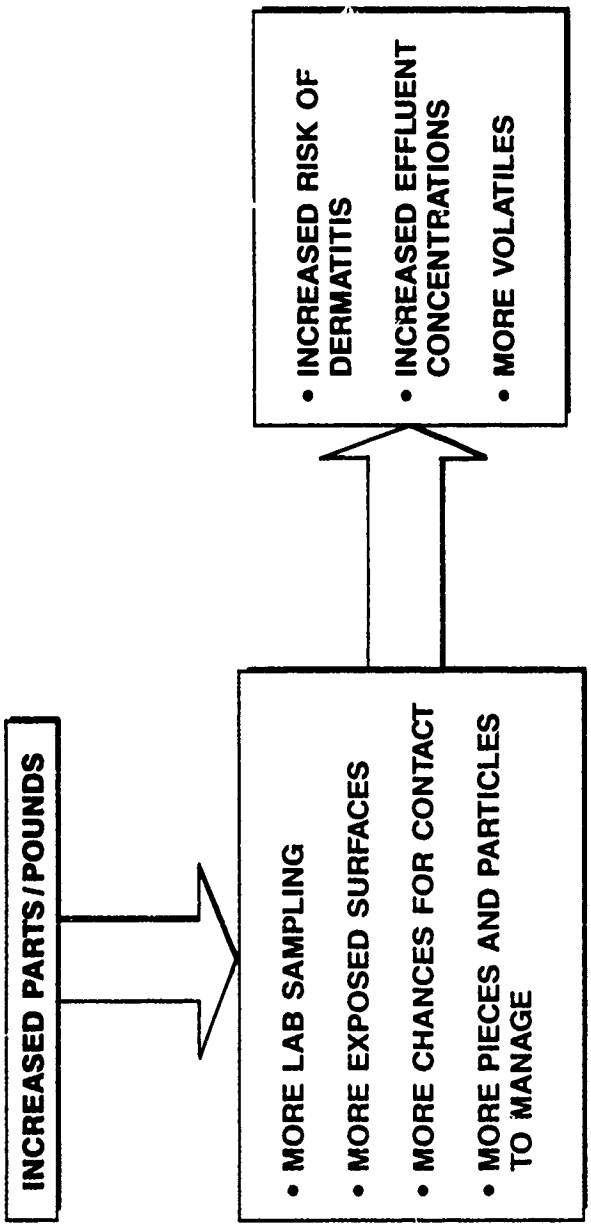


Figure 12. Scale-up will increase exposure.

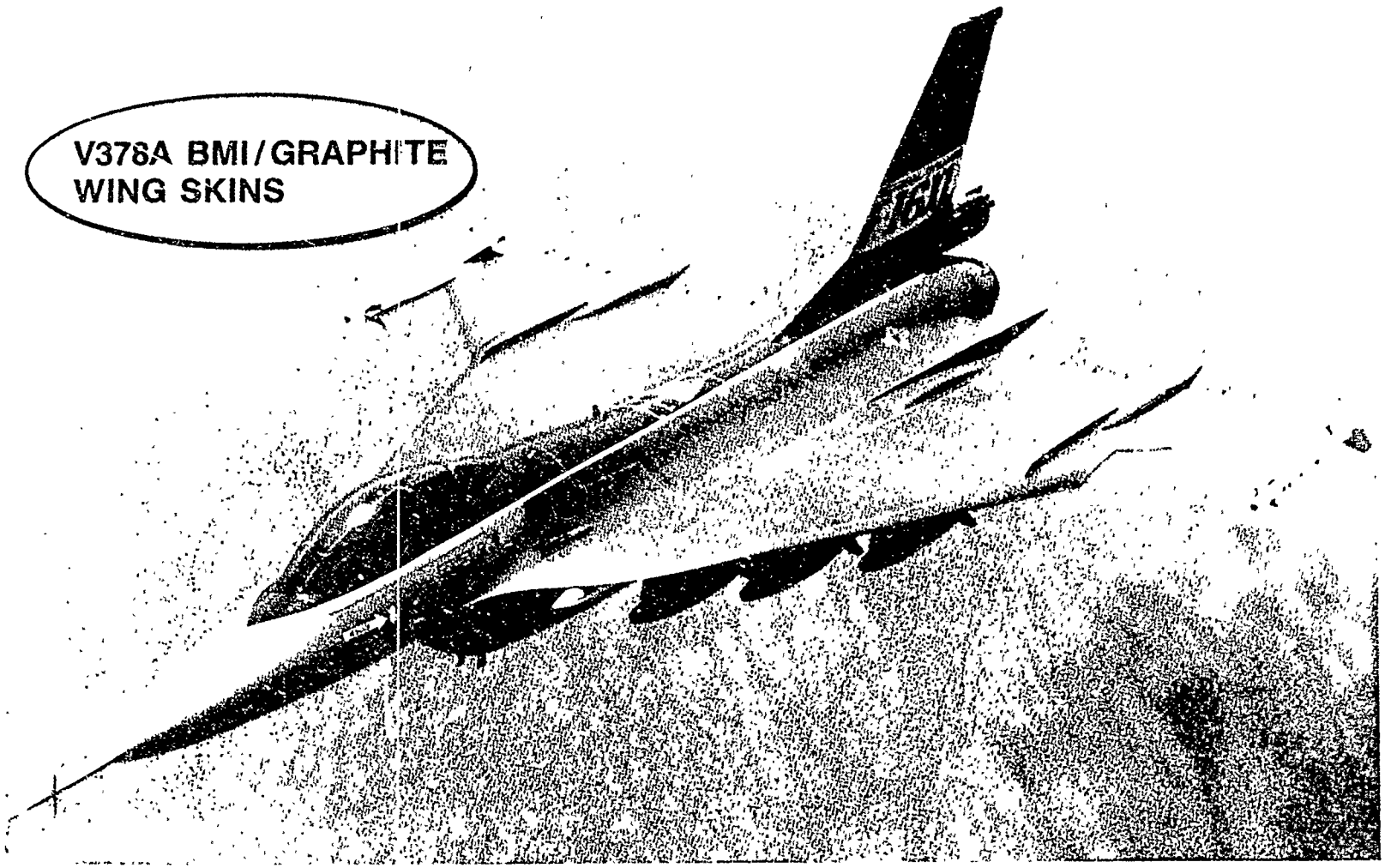


Figure 13. Concern about exposure is not new.

- EFFLUENTS WERE DETERMINED BY GD/FW, HITCO AND ARMCO
  - Divinylbenzene (DVB)
  - Ethyl Vinyl Benzene
  - Diethyl Benzene

- WORK AREA CONCENTRATONS WERE DETERMINED BY GAS CHROMATOGRAPHY
  - Silica Gel Sampling
  - Charcoal Tube Sampling

- DVB WAS THE MAJOR EFFLUENT (<1 ppm)

NO HEALTH HAZARDS HAVE BEEN DETECTED

Figure 14. V378A's distinctive odor was investigated.

- CAREFUL ATTENTION TO MATERIAL SAFETY DATA SHEETS
  - Accuracy
  - Completeness
- EFFLUENT IDENTIFICATION/MONITORING
  - Composition
  - Concentration
- DEVISE REASONABLE AND EFFECTIVE HANDLING PRACTICES
  - Protection
  - Procedures
- OPEN AND COMPLETE INFORMING OF WORKERS

Figure 15. Several actions are advisable.

SUMMARY

We foresee that new composite materials will provide quantum strides in remarkable new aerospace processes performance. Furthermore, we perceive they will allow us to eliminate many traditional hazardous wastes to the environment from our current product lines. Attendant occupational risks from composites are identifiable and manageable, and we are committed to that posture (Fig. 16).

ACKNOWLEDGMENTS

Critique and technologies were provided by Bill Kaarlela and Bill Rosenthal.

- COMPOSITES PROVIDE REMARKABLE PRODUCT PERFORMANCE
  - ✓ Lightweight
  - ✓ High Strength
  - ✓ Low Modulus Structures
- OPPORTUNITIES TO ELIMINATE HAZARDOUS WASTES
  - ✓ Metal Degreasers
  - ✓ Acid Metal Deoxidizers
  - ✓ Chromates From Paints
  - ✓ Acid Surface Treatments
  - ✓ Resultant Filter Press Sludge
  - ✓ Chromates From Surface Treatments

CHALLENGE TO MANAGE ISSUES OF

- ENVIRONMENTAL
  - ✓ New Regulations
  - ✓ New Materials
- HEALTH
  - ✓ Worker Protection
  - ✓ Technology Transfer
  - ✓ Monitoring
  - ✓ Appropriate Facilities
  - ✓ Appropriate Protective Clothing
- SAFETY
  - ✓ Autoclaves
  - ✓ Cryogenics

Figure 16. Summary "Composites Technology Overview."

ADVANCED POLYMER MATRIX RESINS AND CONSTITUENTS: AN OVERVIEW OF MANUFACTURING, COMPOSITION, AND HANDLING

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ABSTRACT

This paper examines briefly the manufacture of typical aerospace-grade polymer matrix resins and their prepregs because, by virtue of being chemically reactive substances, the uncured materials present a variety of potential hazards to those who work with them. The degree and the scope of the hazard depends significantly on the particular resin system and how it is handled. Our purpose is to offer an introduction into the diversity of raw materials, how they are combined, and how they are normally handled in the workplace. Others will address aspects of chemical toxicology and industrial hygiene.

INTRODUCTION

Advanced polymer matrix composites are assembled from a variety of combinations of organic polymers and continuous high strength, high stiffness fibers. The fibers, such as glass, carbon, aramid and quartz, are conceptualized easily as shapes rather than structures and chemical compositions. While the chemical compositions of these and other fibers are fairly complex, their structures, chemistry and morphology are fixed under the conditions of molding, assembly and use. Thus, we think about the reinforcements almost exclusively in terms of their physical and mechanical properties, and their content, distribution and orientation in a molded structure. In effect, we view the fibers as we do metallic and wood structures--as essentially passive, load bearing structural elements.

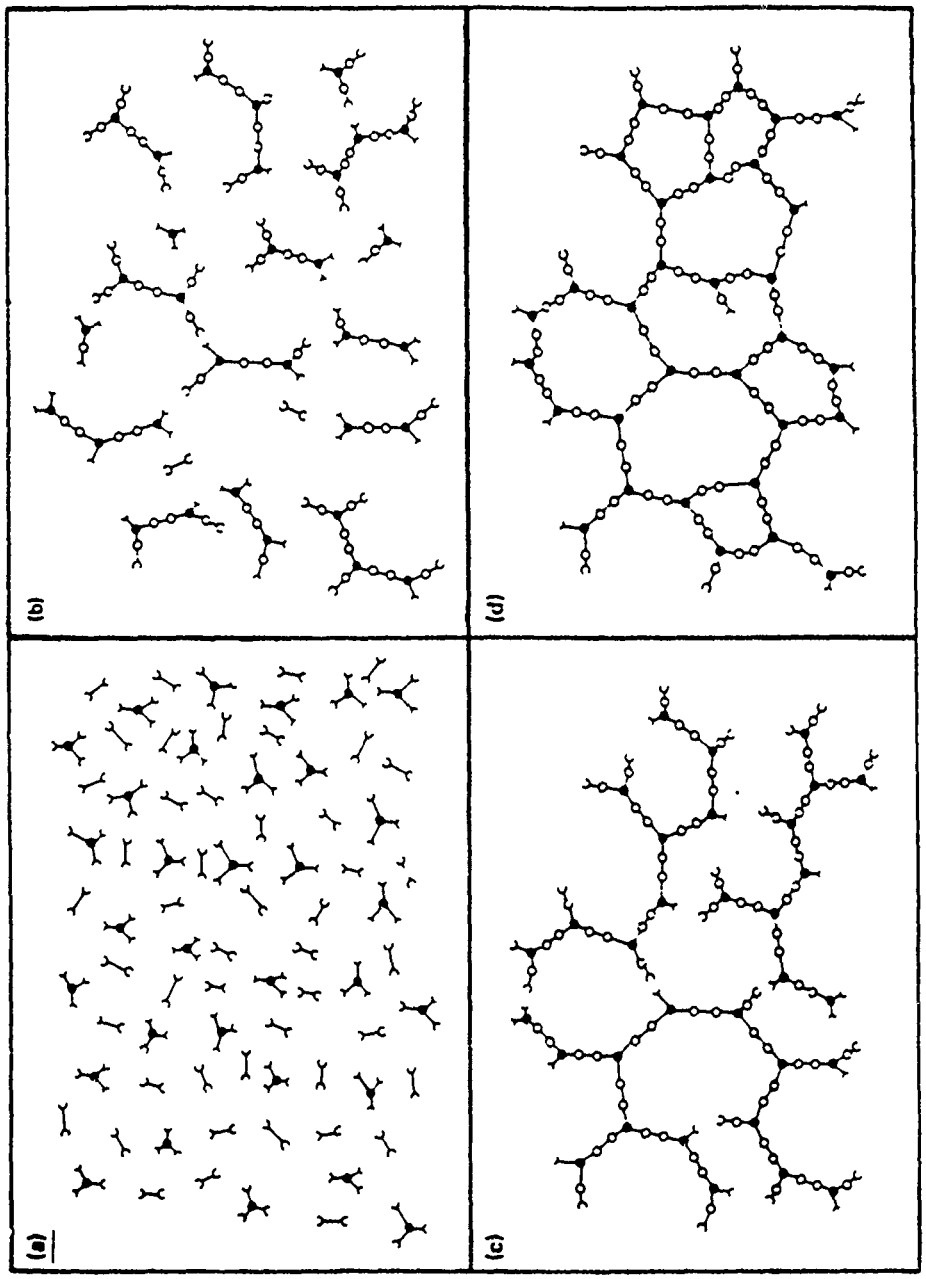
As much as we would like to view the resin matrix in this way, we cannot. The vast majority of matrix resins used for aerospace applications today are complex, chemically reactive systems. The chemical reactivity of what are called thermosetting resins is not accidental. The thermosetting resin systems are designed to be liquids or semi-solids having viscosities low enough to infiltrate all the available volume between fibers and fiber tows to form an homogeneous and continuous matrix or "glue." During impregnation of the reinforcement fibers or fabric, some amount of chemical reaction (advancement) may occur

as illustrated in Figure 1, to form partially polymerized molecules whose gel-like consistency serves to protect the fibers and bind them in a constant spatial relationship during lay-up. With sufficient temperature and time during the molding process, the resin molecules continue to react to form longer linear polymers and subsequently, cross-linked, space-filling solid structures, whose chief function is to transfer stress from one fiber to the next in a fabricated composite part. Once the cure process is complete, that is 100 percent of the chemically reactive groups have combined, the composite is considered chemically inert during further fabrication steps and use.

MANUFACTURE OF PREPREGS

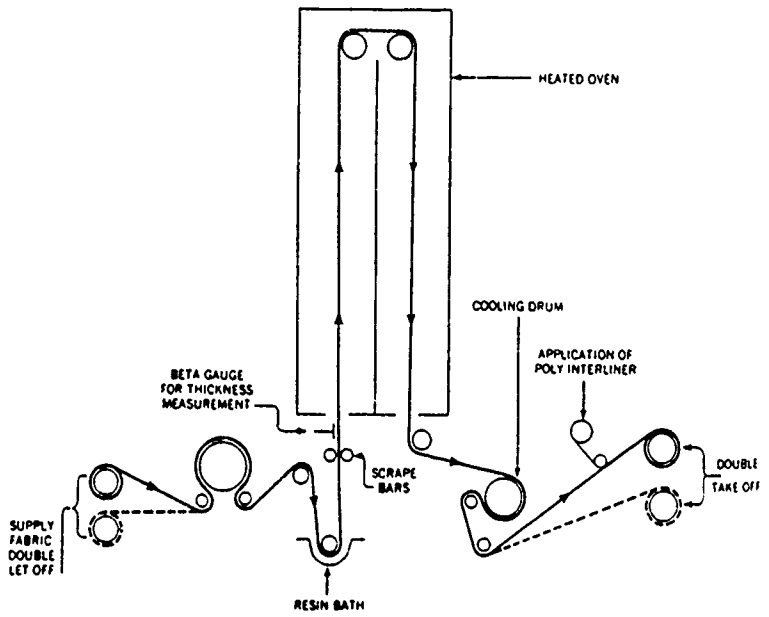
Preimpregnated reinforcements are the simplest and most convenient material forms of the precursors to cured composites. Prepregs take three main forms; namely, woven fabrics, roving, and unidirectional tape. Fabrics and tapes are provided as continuous rolls in widths as much as 72 inches and lengths up to several hundred feet. The fabric or tape thickness constitutes one ply in the construction of a multi-ply lay-up. Impregnated roving is wound onto cores or bobbins and is used for filament winding.

Prepreg manufacturers have developed numerous methods for combining the matrix resins and the reinforcements. Woven fabrics and roving are most commonly produced by dip impregnation, that is, by pulling the reinforcement through a solution of the resin as sketched in Figure 2. The amount of resin picked up by the fibers is controlled by a number of material and process parameters including the density of the reinforcement, resin concentration and viscosity, line tension, the gap between the metering or scrape bars, and the speed at which the fabric or roving is pulled through the resin solution. The wet web is subsequently pulled through an oven where the solvent is driven off and generally incinerated. Heating the resin also causes certain of the constituents to partially react or polymerize to give an advanced or B-staged prepreg. This partial reaction causes the resin viscosity to increase and its tackiness or stickiness to decrease. What appears to be a very simple process is really quite complex in terms of the degree of process control needed to manufacture a product of consistent quality. The standard prepreg properties, namely resin content, flow (viscosity), gel time (reactivity), degree of tack and residual volatiles content are specified to narrow tolerances to achieve the characteristics required by the part manufacturer. The prepregger can exert considerable control over resin reactivity during



R. B. Prime, "Thermosets" in Thermal Characterization of Polymeric Materials, E. Turi, Ed., Academic Press, 1981, p. 437.

Figure 1. Schematic, two-dimensional representation of curing of a thermoset, starting with A-stage monomer(s) (a); proceeding via simultaneous linear growth and branching to a B-stage material below the gel point (b); continuing with formation of a gelled but incompletely cross-linked network (c); and leading finally to the fully cured, C- stage thermoset (d).



H. Reffe, "Prepregs" in Handbook of Fiberglass and Advanced Plastics Composites, G. Lubin, Ed., Van Nostrand Reinhold Co., 1969 (1st Ed.), p. 422.

Figure 2. Typical impregnation in a single tower unit.

B-staging. Depending on the oven temperatures and residence time, a given prepreg system can be manufactured to be very flexible and tacky to permit the construction of shapes having deep and complex profiles, or it can be advanced to be quite stiff and dry to form flat skins on honeycomb panels. The latter prepreg would conceivably have little or no odor from solvents or low boiling reactants. Moreover, little resin would be expected to transfer to a worker's skin or clothing. The former, less chemically reacted prepreg may be expected to pose more of a health hazard to people working with it.

Unidirectional tapes are manufactured by blade or roll casting a semi-solid hot melt resin onto a plastic-coated paper and in either a continuous or subsequent operation, by pressing highly parallel fiber tows into the resin film. This process is shown schematically in Figure 3. Hot melt resins are generally, but not always, made without solvents. Any advancement of the resin is generally accomplished by mixing the components at some elevated temperature and prior to casting it on paper.

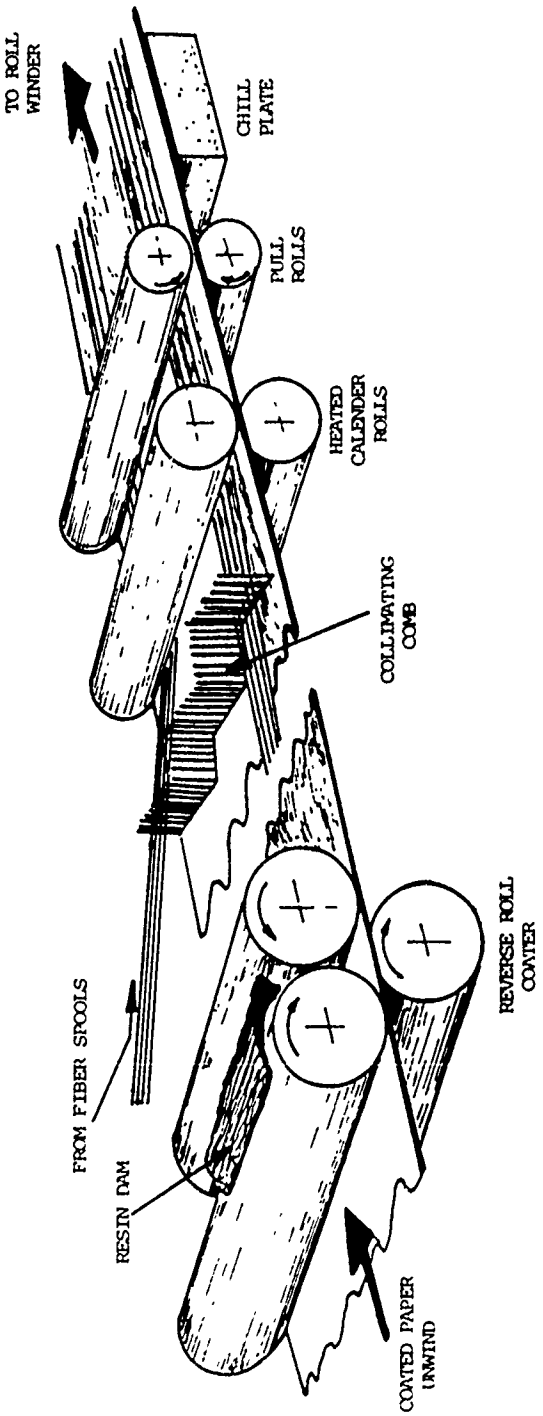


Figure 3. Hot melt prepreg line.

Personnel who dispense, mix and work with resins in bulk quantities are exposed to a large variety of potential health and safety hazards. Prepreggers commonly manufacture many different kinds of products, often simultaneously. The principal hazards involve skin, eye and respiratory contact with such materials as:

- Flammable and highly volatile solvents
- Volatile primary polyamines
- Reactive liquids including glycidyl ethers, styrene & diallylphthalate
- Dust-forming solid amines such as methylene dianiline and meta-phenylene diamine
- Powerful oxidizers including benzoyl peroxide and methylethylketone peroxide
- Corrosive organic acids and acid anhydrides
- Epoxy resins containing small quantities of epichlorohydrin, a strong skin sensitizer
- Toxic dusts from such fillers as antimony oxide and fumed silica.

Given this assortment of materials that can be in the workplace at one time, there is obviously no single or simple way to eliminate chemical hazards. A well-designed and properly ventilated manufacturing environment is of paramount importance. But, so are employee education and the strict, mandatory and constant attention to proper personal protective equipment.

Prepreg manufacturers depend quite heavily on raw material suppliers for education and guidance in the safe handling of commercial and developmental products. Companies such as Shell, Ciba-Geigy, DuPont, Dow and many others have sponsored detailed toxicological studies for many of their products and have made the results available through material safety data sheets, special technical bulletins, product sheets and special seminars.

Polymer Matrix Resin Systems

Advanced polymer matrix resins are systems of materials. They are combinations of a variety of chemical substances, each of which is intended to serve a very specific chemical or physical function. A few systems are so simple as to be nothing more than a partially

formed or living polymer whose increase in molecular weight was quenched by freezing the material. All that is needed subsequently is to impregnate the solution and allow the reaction to continue by applying heat during the cure process. The majority of resin systems, especially polyester and epoxy-based systems, are complex formulations designed using several kinds of polymerizable molecules, one or more catalytic ingredients, one or more solvents and so on to ten to twenty constituents. A more complete listing of material types that could comprise an advanced matrix resin is as follows:

- Monomeric and/or oligomeric resin(s)
- Curing agent or coreactant(s)
- Reactive diluent
- Catalyst(s)
- Promotor and accelerator
- Inhibitor
- Fire retardant
- Smoke suppressant
- Viscosity control agent
- Air release agent
- Pigments
- Fillers

This list is not exhaustive.

The various reactive and inert components can be combined in different ratios to achieve specific sets of resin processing behaviors, prepreg characteristics and end-use or performance-based properties of the cured composite.

In the discussion below, we will describe some of the more common types of thermosetting resin systems and their components. The reader should bear in mind that this topic is voluminous. Numerous texts, papers and encyclopedia articles are available for

detailed chemistry and discussions of processing. All that can be done here is to paint the subject with a very broad brush to illustrate some basic principles.

With the possible exception of certain of the polyimide matrix resin systems, most thermosetting resins are formulated by starting with monomeric and oligomeric raw materials produced in large batches by others. The raw materials are readily available, and their identities are common knowledge within the industry. The prepreggers' proprietary art and expertise lies in knowing what materials to combine and in what quantities and under what conditions to achieve specific customer requirements. A few of the compositions of matter and processes are patented. Most are held as trade secrets for competitive advantage. The resin types used most commonly for advanced composites are shown in Figure 4, along with sketches of the chemical functionality from which the resins derive their names.

Epoxy Resins

An epoxy formulation is principally a mixture of molecules containing one to four epoxide groups and a coreactant called the curing agent. The 1,2-epoxide group is exceptionally chemically reactive and will react with a broad class of chemical types including: acids, anhydrides, amines, alcohols, phenols, mercaptans, and water. A typical multi-step reaction between an epoxy and a primary amine is illustrated in Figure 5.

Several of the epoxies and curing agents used most commonly for aerospace applications are illustrated in Figures 6 and 7. The diepoxides give linear copolymers which tend to be flexible. The epoxies containing three and four epoxide groups give rigid, three dimensional and space-filling copolymers that emphasize high stiffness and service temperatures as high as 350-400°F. Many epoxy systems can be partially cured using heat alone. Catalysts are necessary to cause 100 percent of the reactive groups to combine and participate in cross-linking during molding.

Unsaturated Polyester Resins

The polyester resins used for advanced composites contain olefinic or double bonds in the molecular backbone to facilitate addition-type cross-linking reactions. The unsaturated polyester is obtained from the resin manufacturer as a low molecular weight (1,000-4,000) prepolymer, generally assembled from three or more monomeric materials. These are

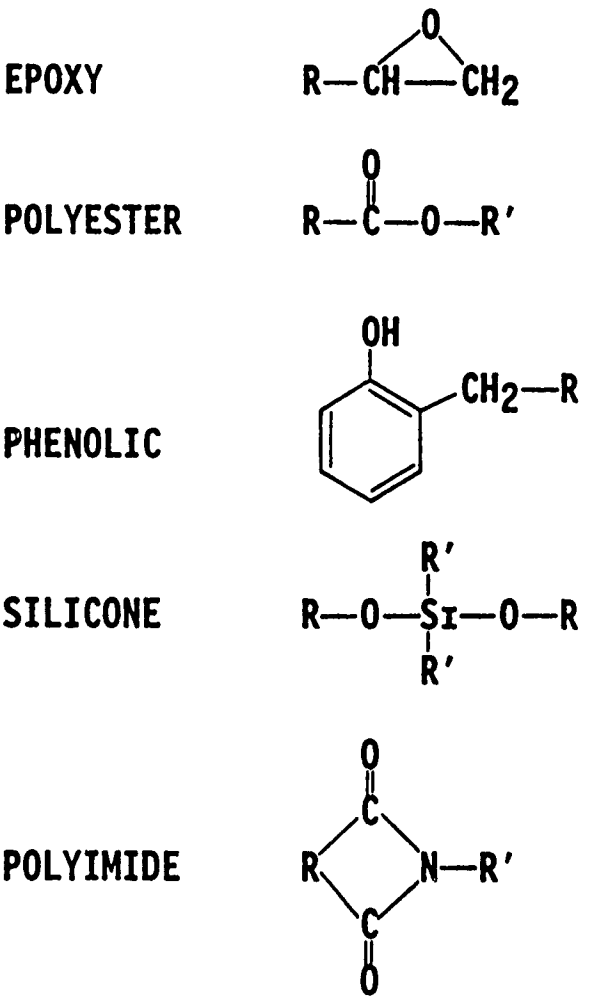


Figure 4. Matrix resin types.

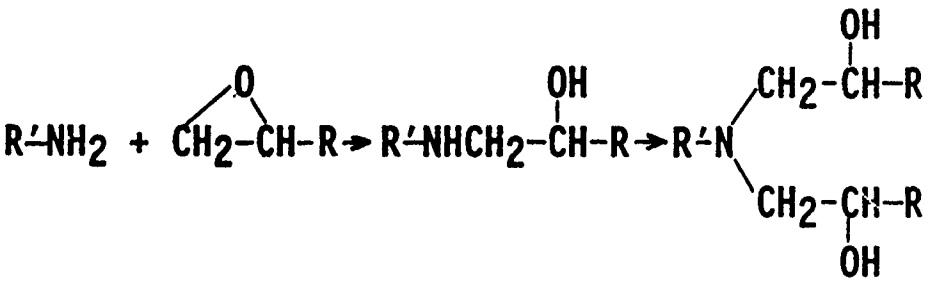
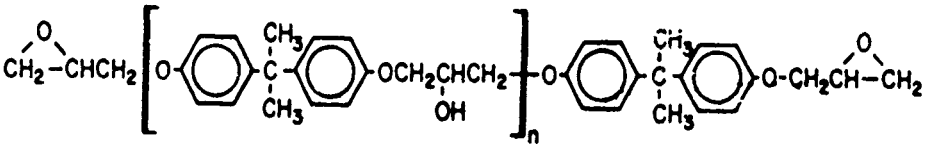
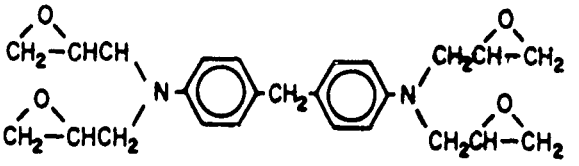


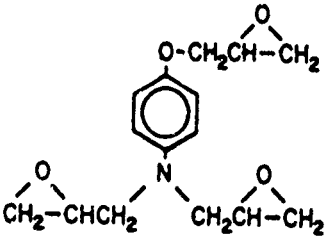
Figure 5. Epoxy-amine reaction.



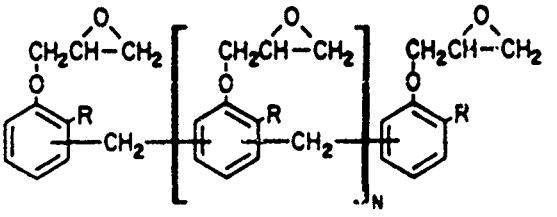
Diglycidyl ether of Bisphenol A



Tetraglycidylmethylenedianiline



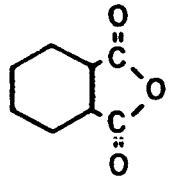
Triglycidyl-p-aminophenol



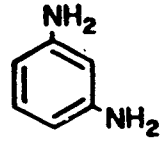
An Epoxy Novalac (Araldite ECN 1235)

Adapted from illustrations in University of Delaware Composites Design Guide, Volume 3, Processing and Fabrication Technology, 1984.

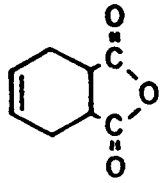
Figure 6. Selected epoxy resins.



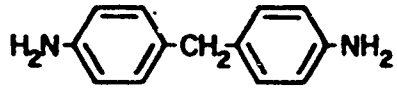
Hexahydrophthalic anhydride



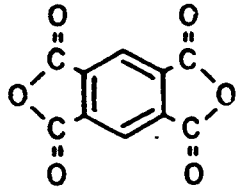
meta-phenylene diamine



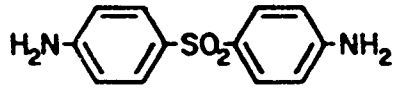
Tetrahydrophthalic anhydride



4,4'-Methylene dianiline



Pyromellitic dianhydride



4,4'-Diaminodiphenyl sulfone

Adapted from illustrations in University of Delaware Composites Design Guide, Volume 3, Processing and Fabrication Technology, 1984.

Figure 7. Selected epoxy curing agents.

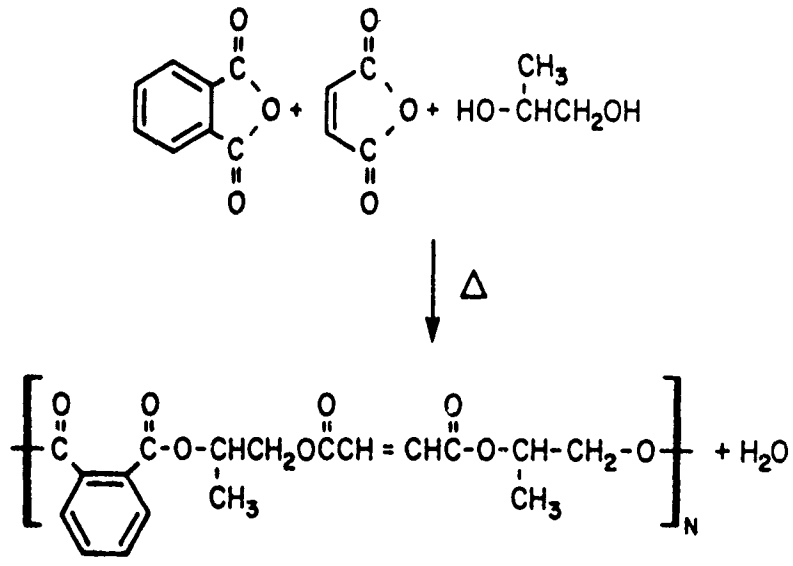
typically an aromatic acid for molecular rigidity, an acid or anhydride containing the double bond and a glycol which corresponds loosely to the curing agent in epoxy-based chemistry The formation of a common type of unsaturated polyester is illustrated in Figure 8. This figure also shows how substances as styrene and diallylphthalate are used to cross-link the linear polymer chains.

Phenolic Resins

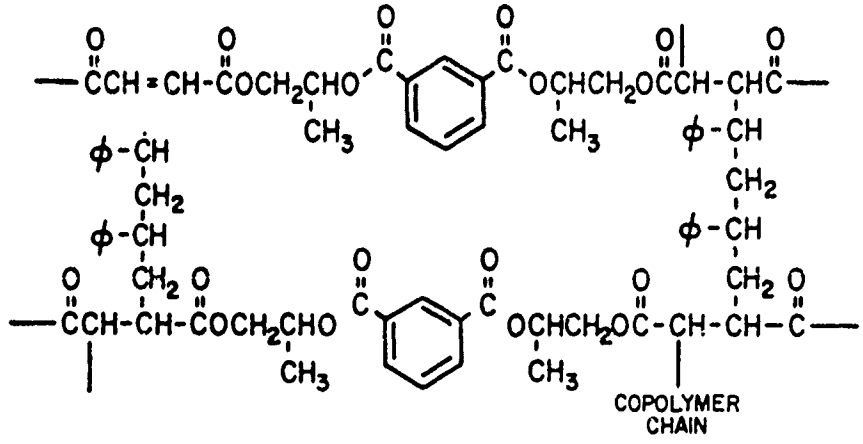
The most generally useful phenolic matrix resins are those formed from phenol and formaldehyde. There are two kinds of phenolic resins. The novalac type is formed under acidic conditions and where the quantity of formaldehyde is not sufficient to effect complete cross-linking. The resole type is more applicable to prepregs. The polymer is formed under alkaline conditions where there is a slight excess of formaldehyde. This chemistry is illustrated in Figure 9. Approximately 95-98 percent of the formaldehyde is chemically combined in the polymer backbone at the time the prepreg is manufactured. The small residual quantity is consumed during the cure reaction in the formation of the methylene ($-CH_2-$) bridges or cross-links which produce the very rigid matrix structure.

Polyimide and Bismaleimide Resins

A polyimide is formed by reacting an aromatic diamine, such as methylene dianiline, with one or more acid anhydrides or esters as illustrated in Figure 10. The example given is a variety of PMR-15, a very stiff polymer that is capable of sustaining temperatures as high as 600°F. The monomeric constituents are dissolved in methyl or ethyl alcohol, and prepregs generally contain three to five percent free alcohol prior to cure. The linear polymer forms through a condensation reaction that produces volatile alcohol and water. Cross-linking proceeds by addition reactions at the double bonds. The primary nitrogen groups of the methylene dianiline are so reactive that the diamine and nadic ester can react to form low molecular compounds during refrigeration of resin solutions and prepregs at temperatures as low as 40°F. Additional polyimide constituents are shown in Figure 11.



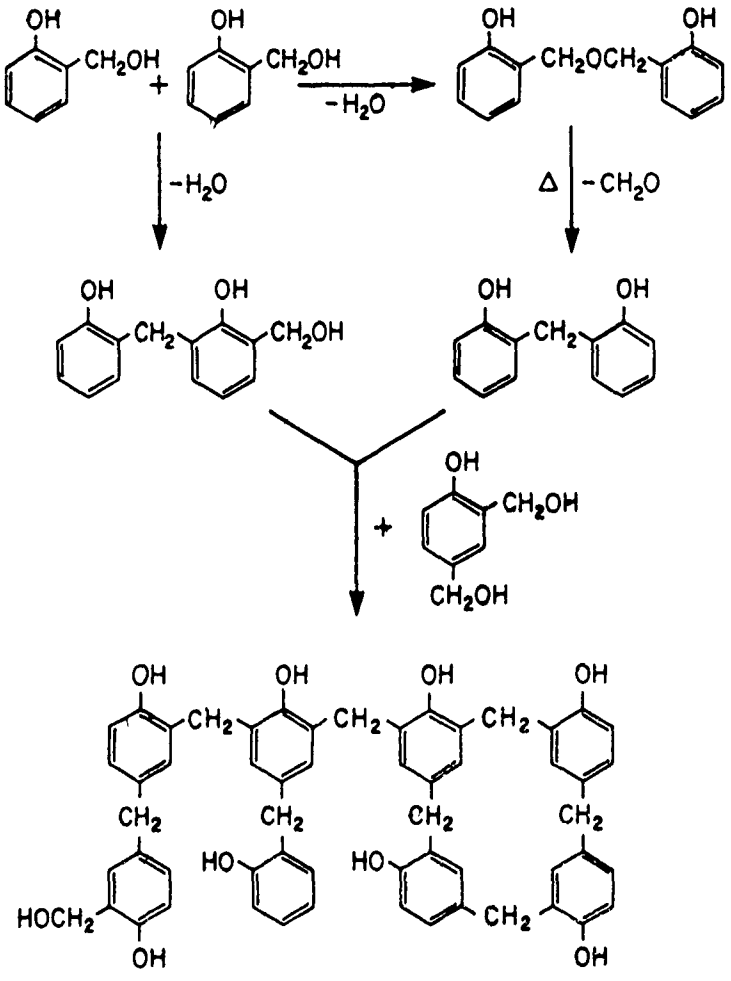
(a)



(b)

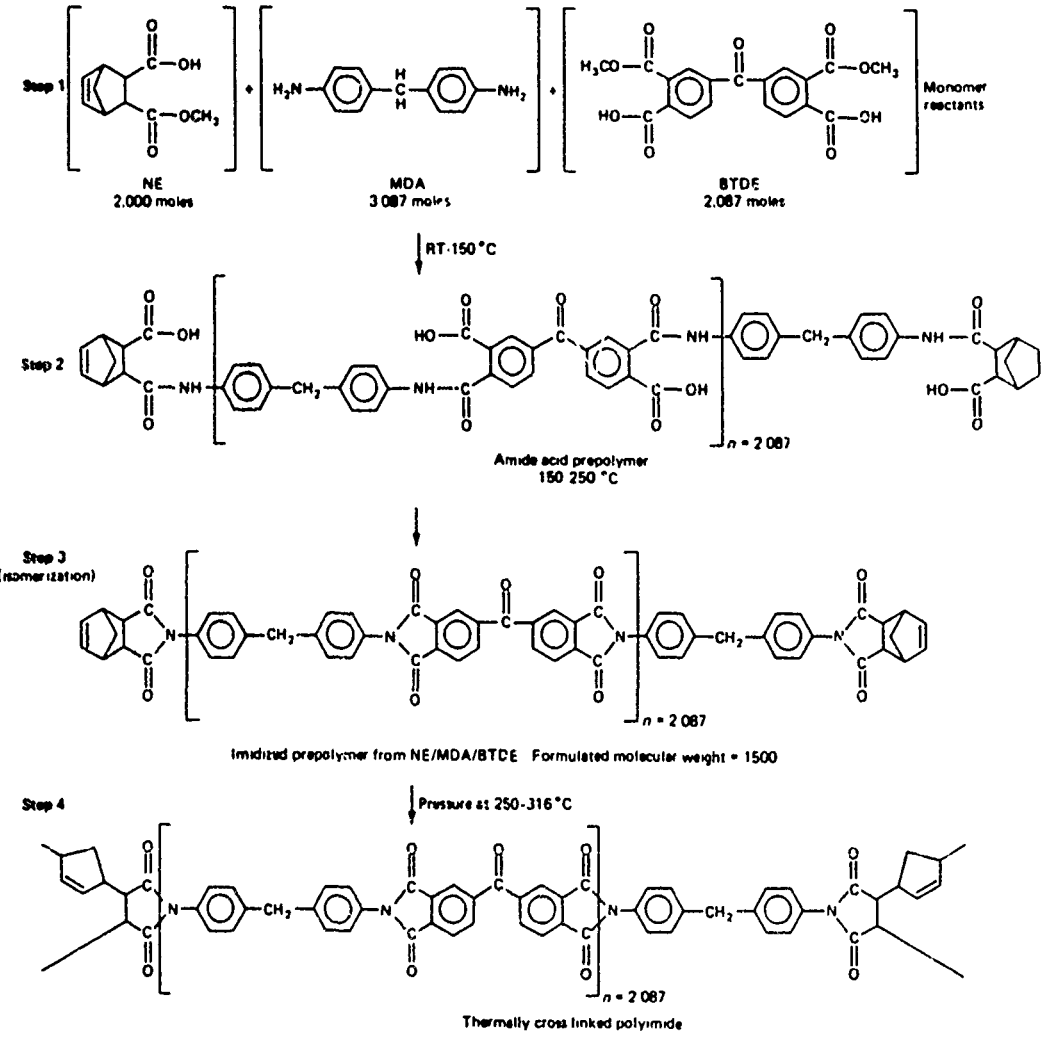
Adapted from illustrations in University of Delaware Composites Design Guide, Volume 3, Processing and Fabrication Technology, 1984.

Figure 8. A typical unsaturated polyester matrix resin (a) and the cross-linking reaction with styrene monomer (b).



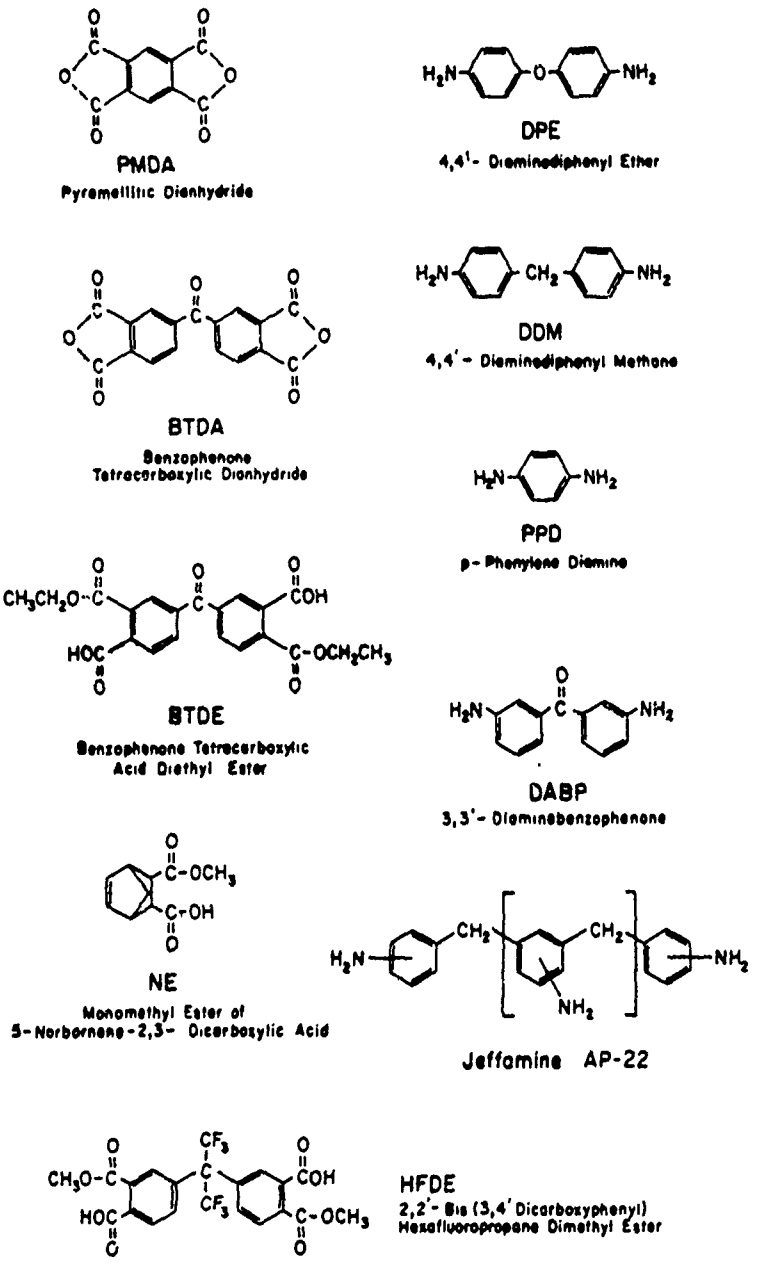
Adapted from illustrations in University of Delaware Composites Design Guide, Volume 3, Processing and Fabrication Technology, 1984.

Figure 9 Formation of a phenol-formaldehyde resin.



D. A. Scola, "Polyimide Resins" in Engineered Materials Handbook, Volume 1, Composites, ASM International, 1987, p.82.

Figure 10. PMR-15 polymerization and cross-linking reactions.



Adapted from illustrations in University of Delaware Composites Design Guide, Volume 3, Processing and Fabrication Technology, 1984.

Figure 11 Constituents for polyimide matrix resins.

Handling Matrix Resins and Prepregs

Very few of the constituents used in contemporary composite systems are known to be carcinogenic or mutagenic to humans. Of the various constituents, probably the most toxic class to the body are the amines owing to their chemical similarity to portions of amino acids and proteins. The organic solvents, including alcohols and ketones, are especially dangerous because they can facilitate the entry of toxic materials into the skin and organ systems. Some, as methyl alcohol, are poisonous, and all are capable of extracting fat from the skin. Moreover, most of the solvents employed are highly flammable. This being stated, it is important to realize that the availability of such solvents in prepregs is quite low, typically less than two percent.

The amines and acid anhydrides comprising many of the epoxy and polyimide systems can be very corrosive to skin, eyes and mucous membranes. These materials are capable of causing severe burns to someone carelessly handling the raw materials in bulk. It is extremely unlikely, however, for one handling prepreg to contact any given ingredient in sufficient quantity to produce significant damage.

The catalysts, accelerators and promotors used especially in unsaturated polyester resins are dangerous in their neat form because they are powerful oxidizers. Such materials include peroxides and transition metal complexes. Their concentration in formulated matrix resins and prepregs is of the order of one percent, so the potential for damage is quite low By far the greatest danger presented by formulated resins in general is allergic dermatitis from repeated skin contact. Dermatitis may be as mild as redness and itching of both exposed and non-exposed portions of the body. It can also be quite severe when the allergic reaction takes the form of asthma in particularly sensitive individuals Once an individual is sensitized, only minimal contact with an ingredient or combination of ingredients is needed to induce an allergic reaction.

The diversity of polymer matrix resin systems and prepregs is simply too broad to suggest specific procedures for handling them. However, there is one guiding principle that is true for dealing with chemically reactive materials, and that is: without exposure, there can be no hazard. Thus, every reasonable precaution should be taken to prevent contact of these materials with the body. In a fabrication shop, this means essentially that workers must never touch resins and prepregs with unprotected hands, they must never allow gloves and contaminated clothing to touch their face, eyes and other exposed skin, and they must

not breathe volatile matter and dust given off by or from these materials. It cannot be stated much more simply than this. A worker should no more readily contact an uncured matrix resin or prepreg than he or she put an unprotected hand in a chromate plating bath or operate a stamping press or welding torch without suitable protection.

Ferro Composites utilizes a wide variety of engineering, administrative and personal controls to minimize or eliminate exposures to chemical raw materials and prepreg products as they move through the various analytical, manufacturing, testing and packaging operations. Implementation of the Hazardous Materials Information System (HMIS) has been particularly effective for quickly alerting chemical operators and technicians to specific hazards and to the kinds of personal protective equipment needed. Computer-generated HMIS labels are placed by appropriate personnel on raw material containers before the material is tested or used in the plant as illustrated in Figure 12. The printed labels give numerical ratings for health, flammability and reactivity hazards posed by each chemical. The label also indicates, by letter, the set of protective equipment required. This letter is associated with pictorial representations of the protective equipment on colorful wall charts placed in all materials storage, manufacturing and laboratory areas as illustrated in Figure 13.

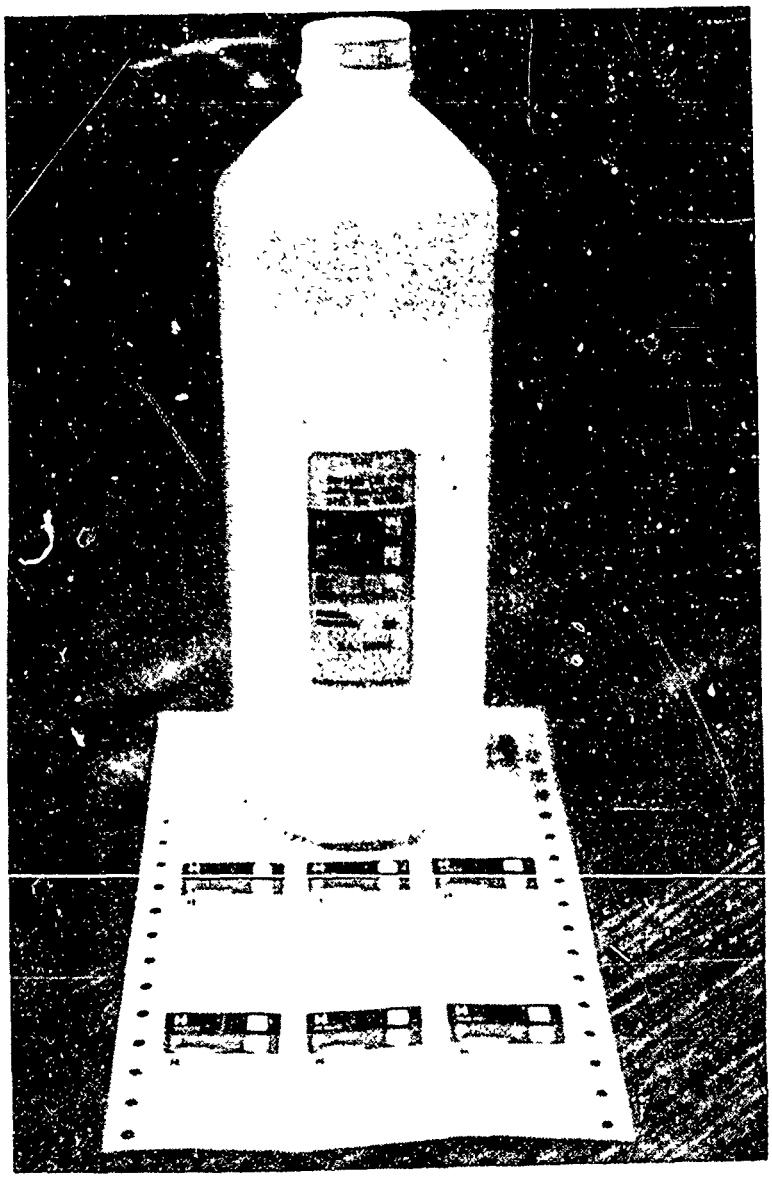


Figure 12. Computer-generated HMIS labels

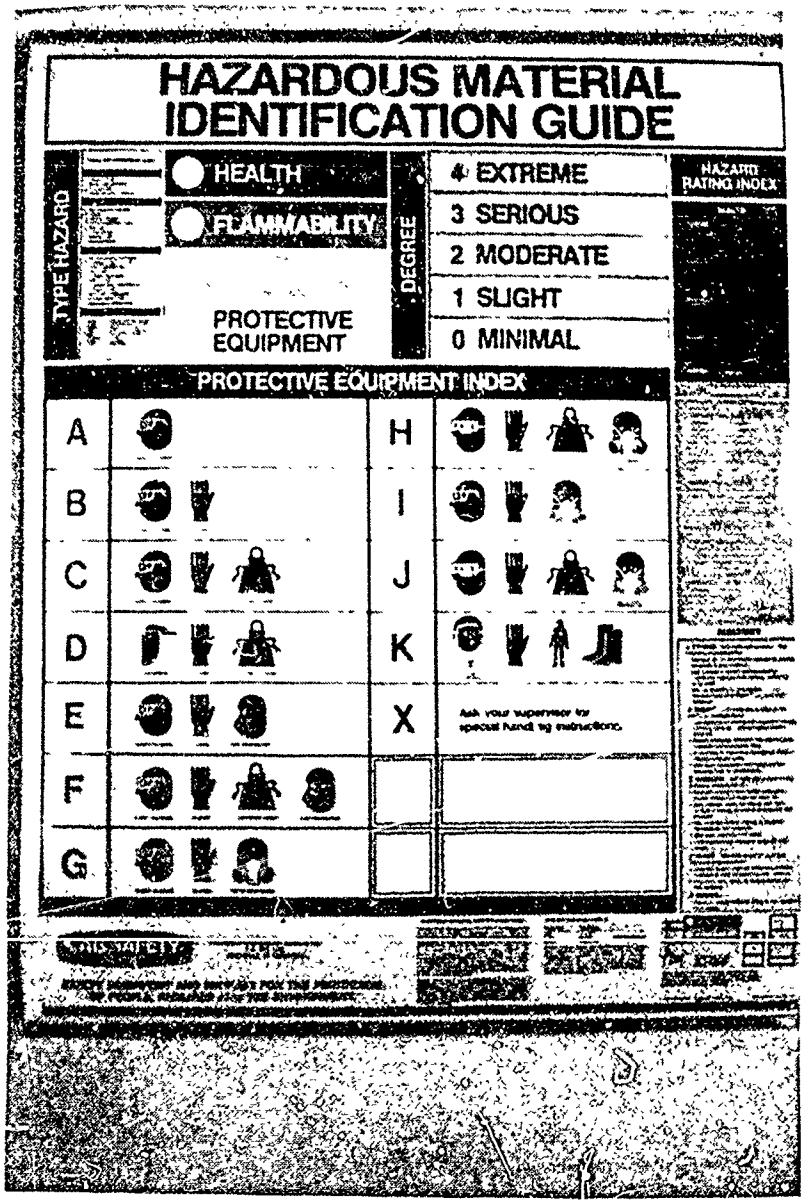


Figure 13 Wall charts placed in all materials storage, manufacturing and laboratory areas.

COMPOSITE PART FABRICATION, HANDLING, AND MACHINING

Anthony A. Faoro

General Dynamics, Fort Worth, Texas

ABSTRACT

General Dynamics - Fort Worth Division is a fully integrated aircraft manufacturing facility. Over 257,700 square feet of floor space and 390 employees are dedicated to the production of composite and bonded structures for the F-16 fighter and spare parts for the F-111. Through 1987, the F-16 program processed 496,781 pounds of pre-impregnated (prepreg) graphite/epoxy composite tape. Although many of the composite components on the F-16 are made from graphite/epoxy prepreg; fiberglass/epoxy prepregs, fiberglass/epoxy wet layups, fiberglass/phenolic wet layups, fiber reinforced graphite/epoxy molding compounds and other reinforced polymeric components are manufactured at the Fort Worth Division.

The following photos and text describe several applications of the three main steps in composites manufacturing and the interaction of the human element in each step. Layup (the placement of composite material on to the part mold) is illustrated for the fabrication of stabilizer skins and fiberglass covers. Processing or curing (the application of heat and pressure to consolidate the laminate and cross-link the matrix) is illustrated with autoclave, press and oven operations. Machining (drilling, trimming and routing of the processed laminate) is shown for the assembly of stabilizer skins.

This essay is restricted to current F-16 technology and does not show every composites manufacturing method used in the industry. These examples should be a good starting point, as they show the fundamental steps in most composites manufacturing methods.

INTRODUCTION

General Dynamics - Fort Worth Division is a fully integrated aircraft manufacturing facility (Fig. 1) employing composites on its aircraft since the B-36 program. The use of composites expanded through the B-58, F-111 and F-16 programs as materials and manufacturing methods were improved. The wet phenolic, polyester, and epoxy layups of the B-58 radomes and fairings were replaced by pre-impregnated (prepreg) Boron/epoxy in

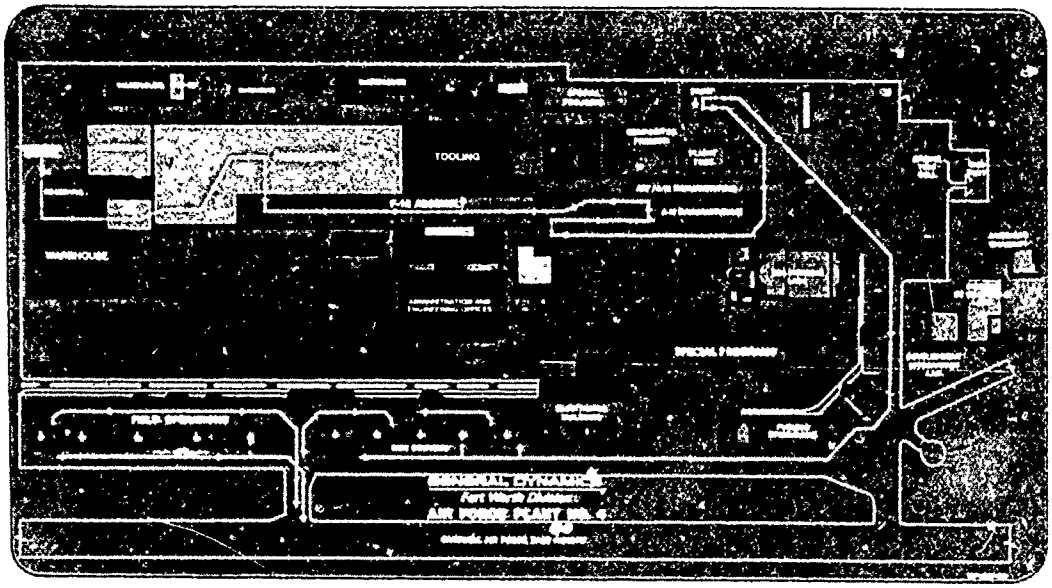


Figure 1. Schematic of Air Force Plant No. 4 - General Dynamics Fort Worth Division.

the F-111 and finally to prepreg graphite/epoxy stabilizer skins on the F-16 (Fig. 2). Most thermoset composite manufacturing procedures are utilized at the Fort Worth Division, even though less than 4 percent of the F-16 touch labor is dedicated to non-metals manufacturing.

The composite manufacturing practices shown in the following text evolved from Fort Worth Division's experience to meet the need of graphite/epoxy composite on the F-16. Other composites manufacturers may have more or different experience, however the basic steps in composite manufacturing (layup, processing/consolidation, and machining) are universally applied throughout the composites industry.

The increasing role of composites in advanced aircraft structure is altering composite materials and manufacturing methods. Examples are presented to increase the awareness of the uninitiated and solicit input from the informed. The following figures simulate current composite fabrication processes for the reader. New materials and procedures may require different controls and practices to address the occupational health aspects of advanced composite manufacturing.

COMPOSITE MANUFACTURING METHODS

Layup: The first step in composite manufacturing is layup. Layup begins with the delivery of prepreg, dry fibers, and raw resin materials. All thermoset composite prepregs are delivered and stored in air tight containers at sub-zero (°F) temperature. Resins are usually supplied in two part mixes. Each part is packaged in a sealed container that may or may not require refrigeration.

In layup, the plies of composite material are placed on to the part mold, trimmed and bagged for consolidation/processing or intermediate refrigerated storage. For wet layups, dry fibers are placed on the forming tool. The resin components are mixed together and the resin is worked into the fibers with plastic spatulas on the forming tool (Fig. 3).

All prepregs are warmed to room temperature inside sealed containers before the seal is broken. After the prepreg reaches room temperature, it is removed from the containers and placed in the forming tool by hand (Figs. 4 and 5) or by the Automated Tape Layer (Fig. 6). The hand laying procedure is the same for fiberglass cloth or graphite tape. Automated layup is restricted to unidirectional tape.

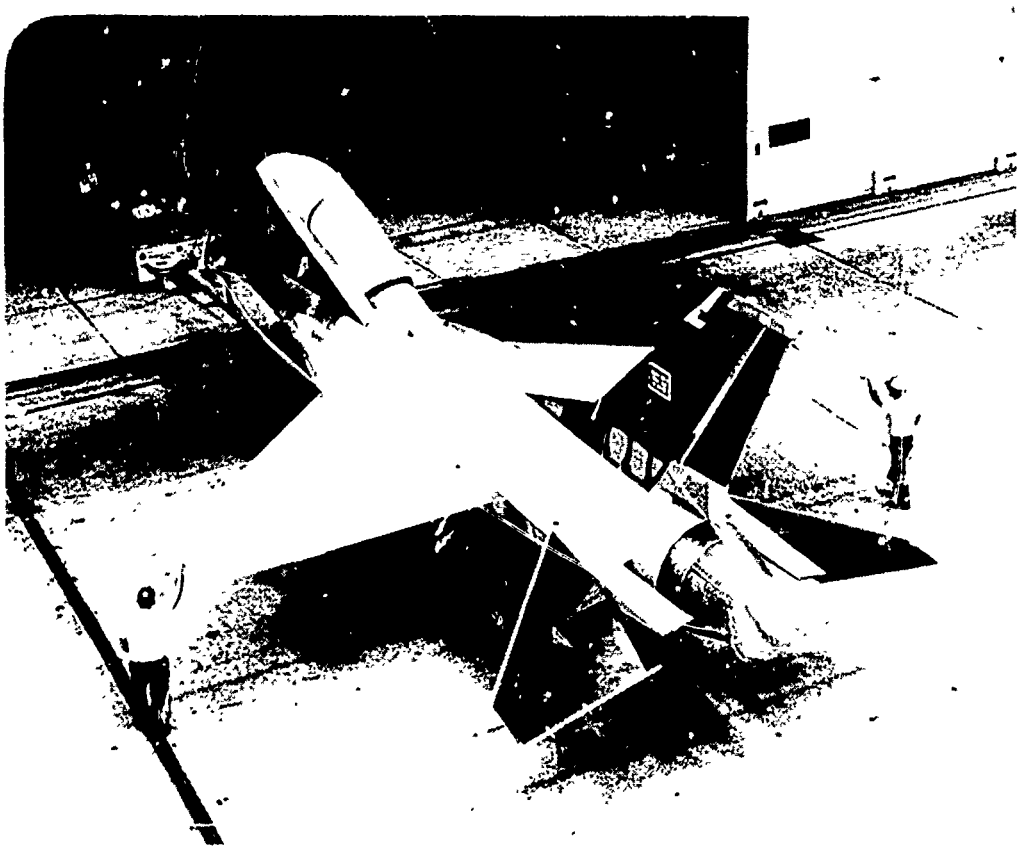


Figure 2. Unpainted F-16 showing the dark graphite/epoxy composite horizontal and vertical stabilizer skins.

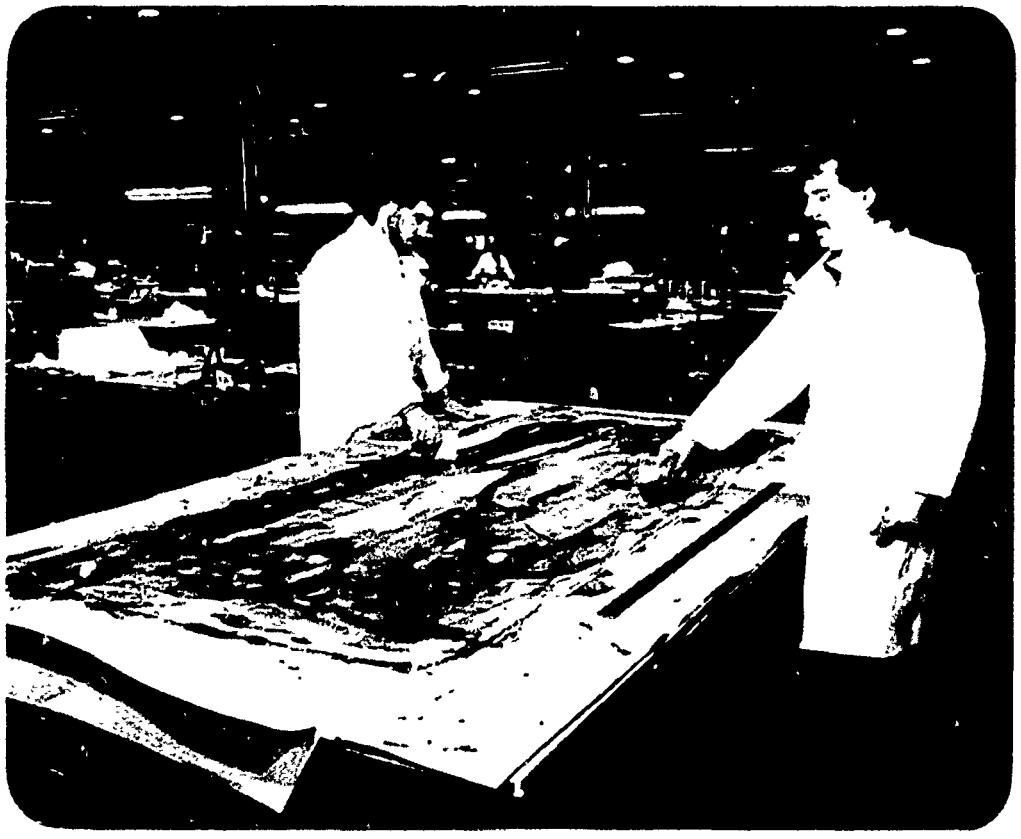


Figure 3. Wet composite layup - woven 181 fiberglass cloth and epoxy resin.

Figure 4. Hand layup - woven 181 fiberglass cloth and epoxy resin prepreg on an aluminum tool.

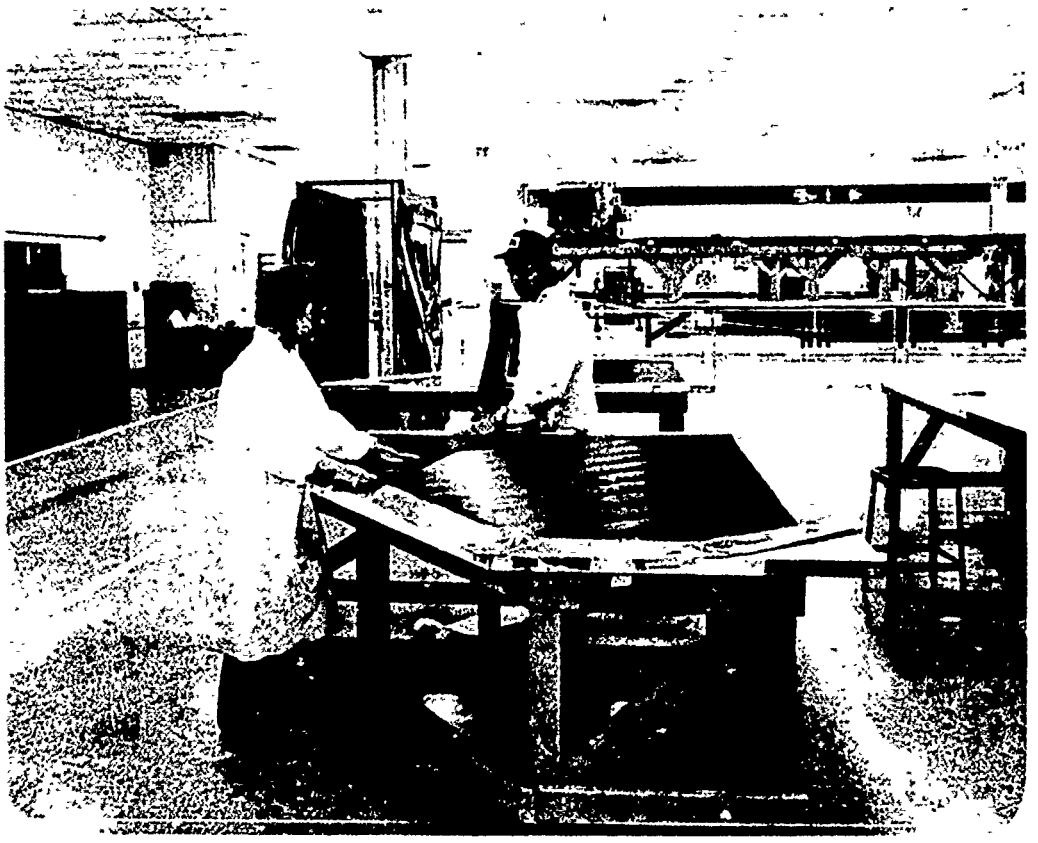


Figure 5. Hand layup - unidirectional graphite tape and epoxy resin prepreg.

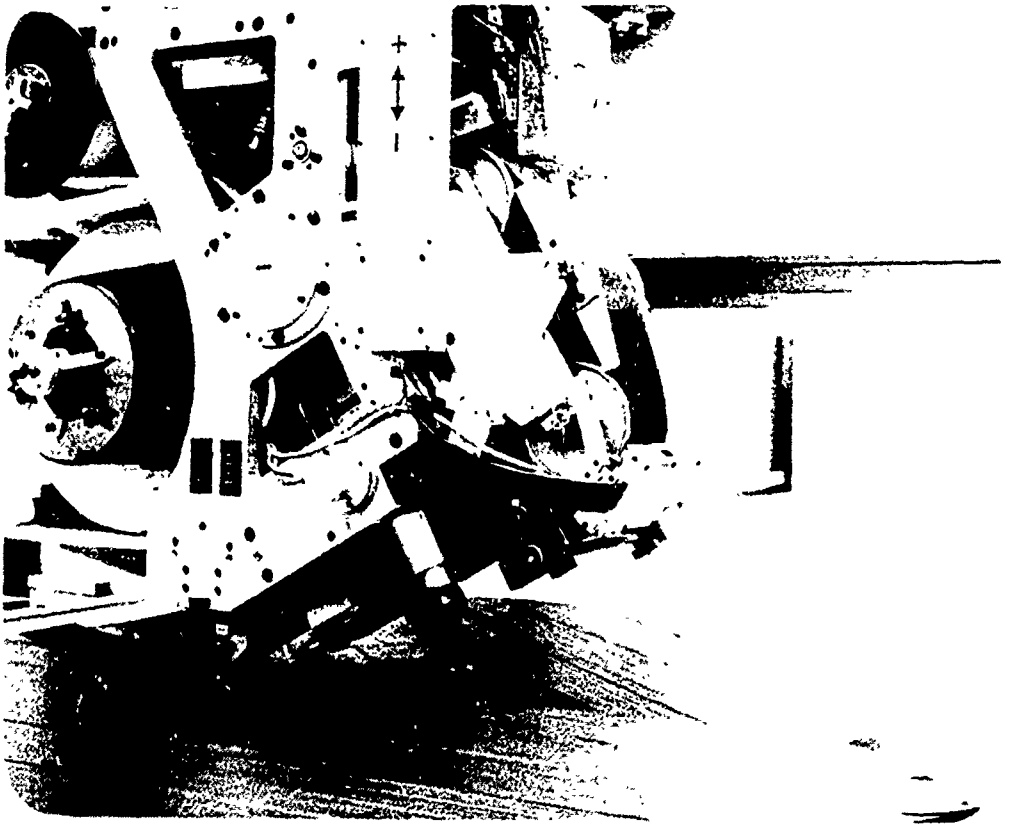


Figure 6. Automated tape layer head - placing graphite/epoxy tape in a horizontal stabilizer skin laminate.

The trimmed laminates can also be placed in a sealed container and stored until the forming tool or consolidation facility is available. The trimming and storage process is usually called kitting and can be accomplished with stacked or unstacked laminates.

When the laminate is placed in the forming tool for processing, it is usually enclosed in an air tight bag. Dry fiberglass and separator films are placed over the laminate (Fig. 7) before bagging. The dry fibers provide channels for escaping volatiles and absorb excess resin during processing.

Alternate Composite Manufacturing Processes: Dry fiberglass over-braiding of insulated ducts (Fig. 8) is an example of an alternate composite fabrication process. The over-braided ducts are heated to 100 °F for 30 minutes then painted with a pigment impregnated phenolic resin (Fig. 9). This phenolic system does not require vacuum consolidation and is returned to the oven without a bag for final processing at 325 °F

Compression molding is another composite manufacturing process that differs from the normal thermoset methods. A pre-weighed mixture of chopped fiberglass and epoxy resin is placed in a heated forming press (Fig. 10). The press is closed and held at 300 °F and 1000 psig. for 30 minutes to consolidate and form the part.

During layup, employees are required to protect their skin from exposure that causes irritation. Impervious cloth or vinyl gloves as well as protective clothing are worn. Prepreg scrap and separator films (backing paper) are disposed of through normal waste disposal. Hazardous reagents of the resins, if any, are placed in the hazardous waste storage for appropriate disposal.

CONSOLIDATION/PROCESSING

Consolidation: In the consolidation/processing step, the composite part is heated to cross-link the matrix and is usually compressed to eliminate voids. The processing method may require multiple steps and use different processing equipment. Throughout the industry, autoclaves (Fig. 11) are traditionally used to process advanced composites. The bagged parts are attached to a vacuum source in the autoclave (Fig. 12). Any volatiles, generated during processing, are drawn off by the vacuum system. The vacuum pumps' exhaust is bubbled through an oil bath prior to release to the atmosphere.

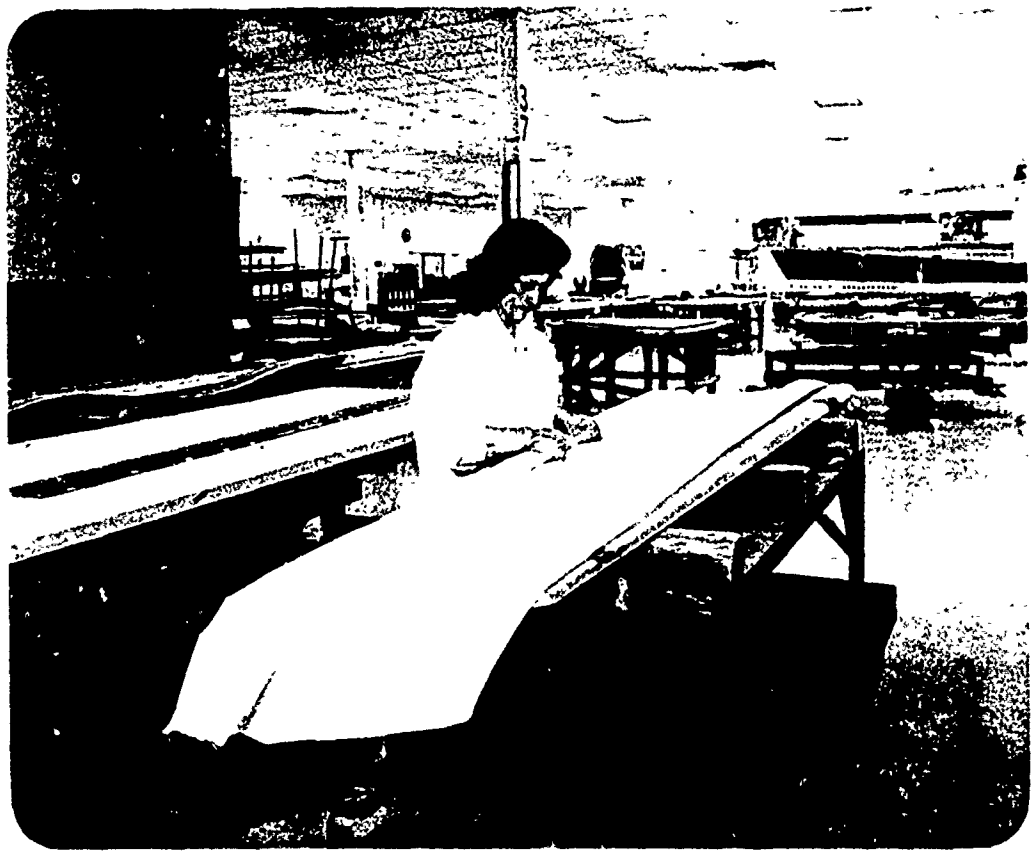


Figure 7. Dry fiberglass cloth "breather" is placed over graphite/epoxy laminate before the bag.

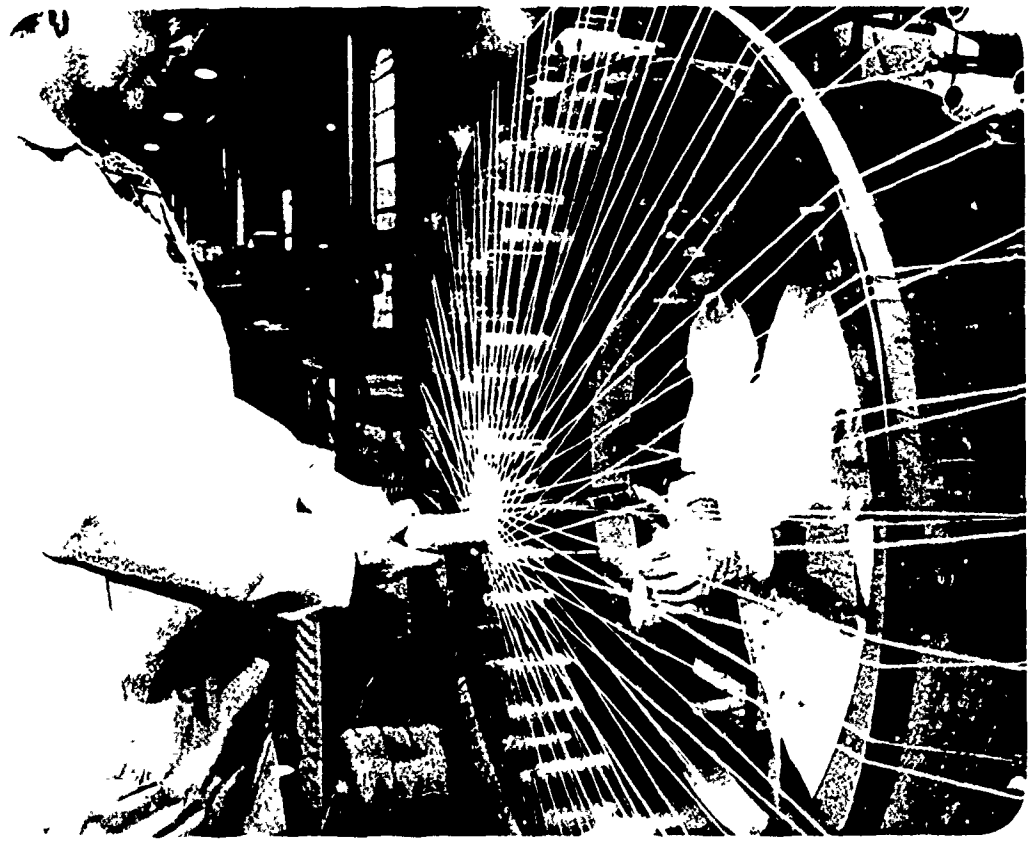


Figure 8. Braiding dry fiberglass over insulated ducts.

Figure 9. Application of pigment impregnated phenolic resin to the fiberglass over-braid.

Figure 10. Loading of the compression molding die with flakes of chopped fiberglass/epoxy prepreg.

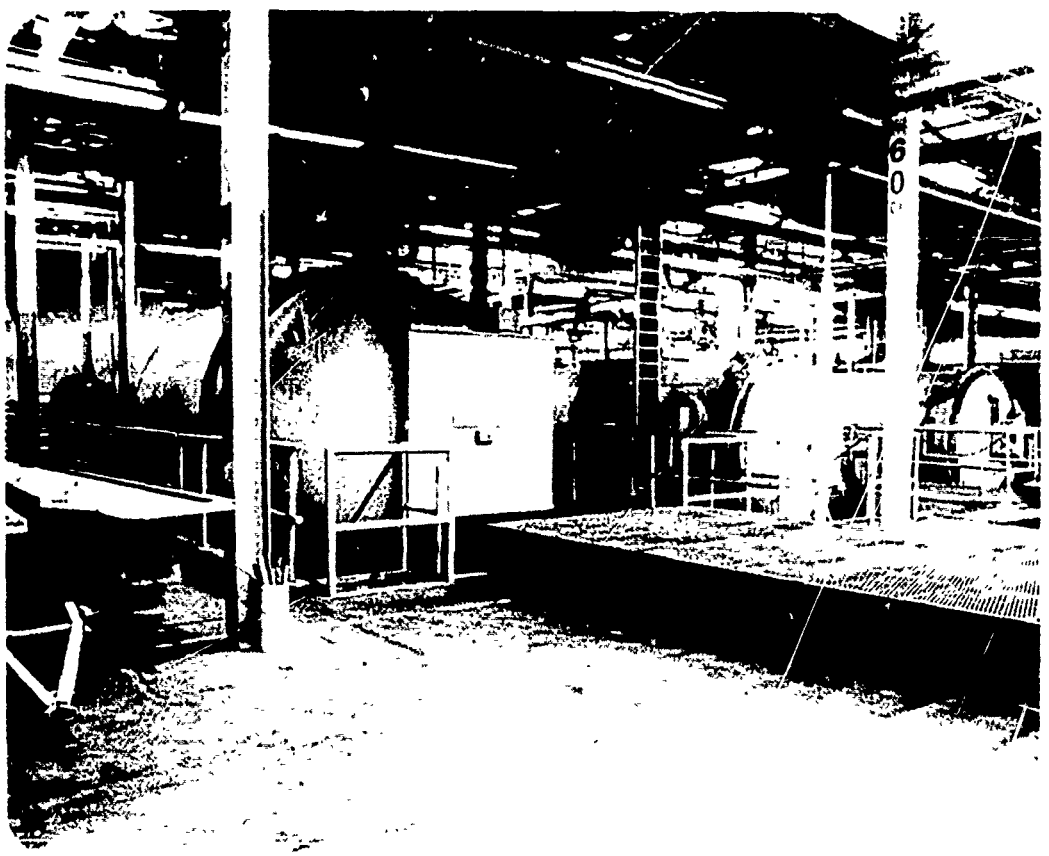


Figure 11. Autoclaves used to process composite parts.

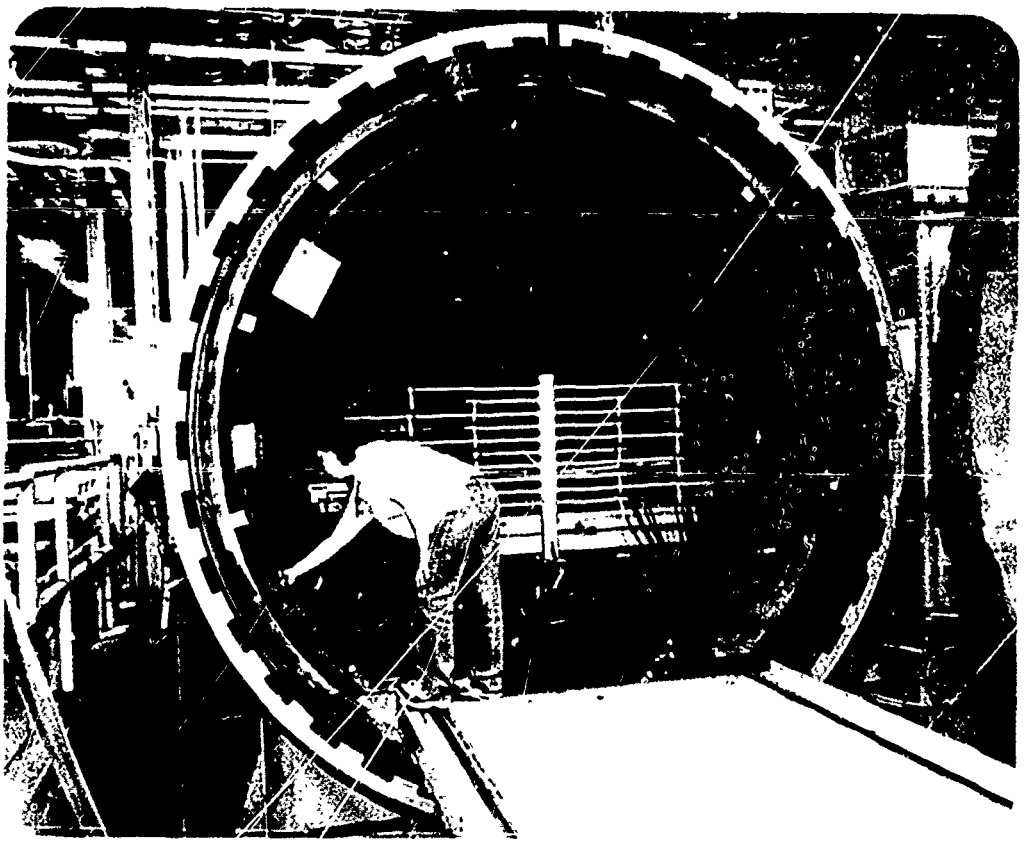


Figure 12. Composite part is connected to a vacuum port in the autoclave.

The autoclave is pressurized during processing to further consolidate the laminate. Nitrogen gas is used in the chamber for safety purposes. The nitrogen is exhausted to the atmosphere at the completion of the cure. The Fort Worth Division also uses cavity presses (Fig. 13) to process thermoset composites and bonded honeycomb parts. Parts processed in the presses are covered by a silicon rubber bag. Vacuum and pressurization operations in the presses are the same as the autoclave with the one exception. Compressed air is used to pressurize the vessel.

Break-out: After the graphite/epoxy skins are autoclave processed, they are removed from the forming tool in an operation called break-out. In break-out, the bag, caul sheet, bleeder, and breather materials are removed from the part (Fig. 14). The used bagging materials (Fig. 15) are collected and disposed of through normal routes to an approved landfill. The partially cured graphite/epoxy parts are sent for additional processing in the post-cure ovens.

Tool cleaning and preparation are performed during break-out. Residual resin is removed from the tool before the tool is cleaned with solvent and treated with a release agent (Fig. 16).

Post-cure: All graphite/epoxy parts undergo additional processing in the post-curing ovens and are inspected before being machined. In the post-cure ovens, the parts are held at temperature, without additional pressure, to fully cross-link the matrix. The fully processed parts are ultrasonically inspected for voids and delaminations prior to trimming.

MACHINING

Trimming: Composite machining is comprised of two operations, drilling and trimming. The composite parts are cut to shape in a room (Fig. 17) specifically equipped with local ventilation for dust collection. The trim room contains routers, saws (Fig. 18) and abrasive water-jets (Fig. 19) used to cut composite parts. The dust collected from these operations is scrubbed and collected in toxic waste containers for appropriate storage. Abrasives from the water-jet are collected and disposed of in approved landfills. The water drains into the sewage system without requiring additional treatment.

Drilling: Composite drilling operations (Figs. 20 and 21) are performed in several locations along the assembly line. The Fort Worth Division is working toward completely

Figure 13. Cavity presses and computer control stations.

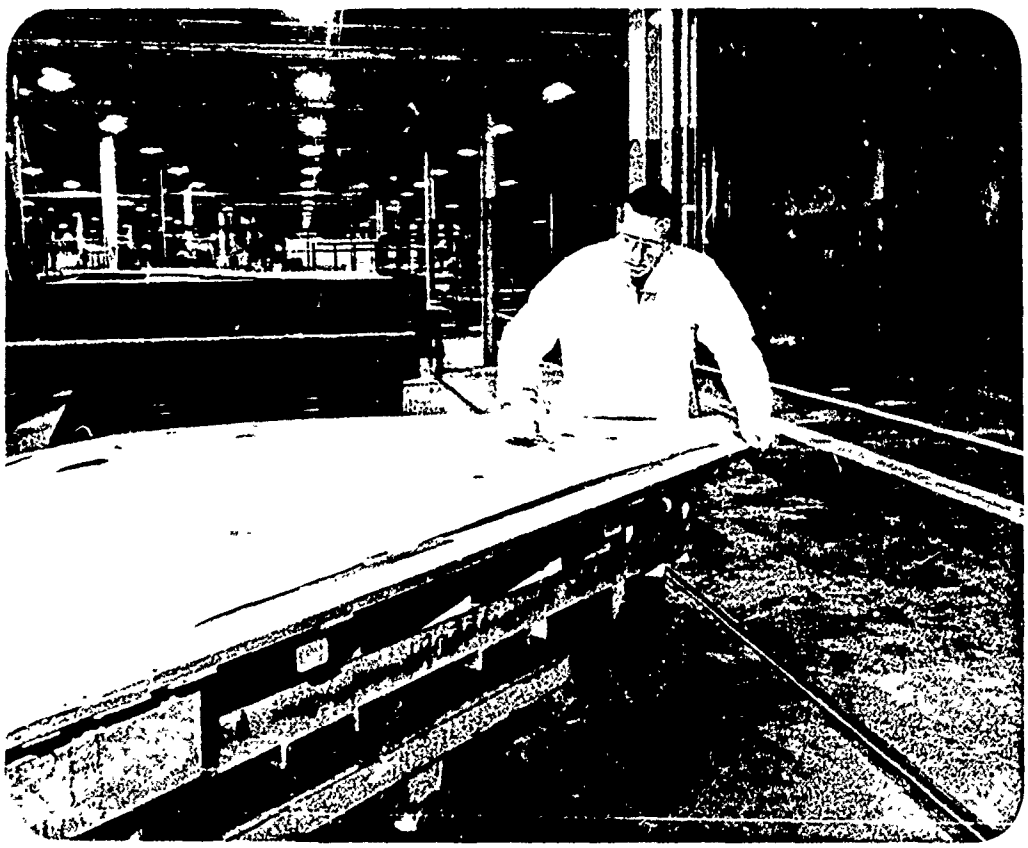


Figure 14. Composite part break-out - removing the caul sheet, and fiberglass "bleeder" cloth from a horizontal stabilizer skin.

Figure 15. Used bagging materials collection bins.

Figure 16. Cleaned forming tools are treated with release agents.

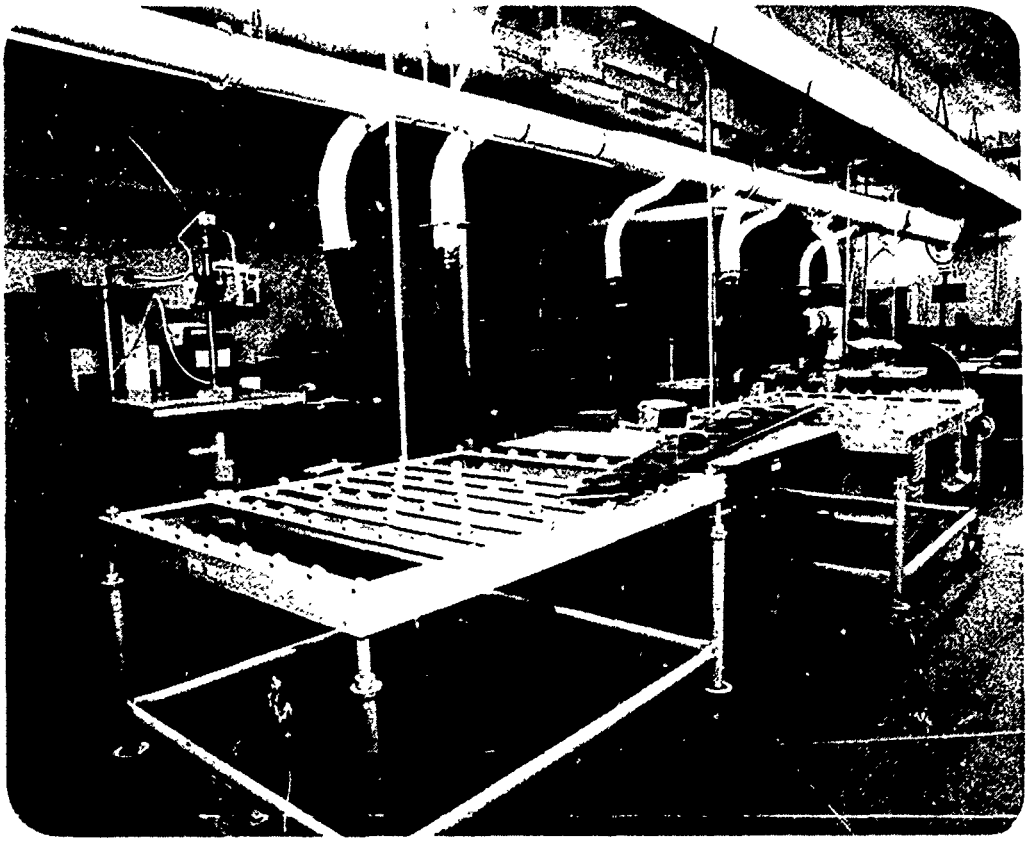


Figure 17. Composite trim room work-stations and dust collection system.

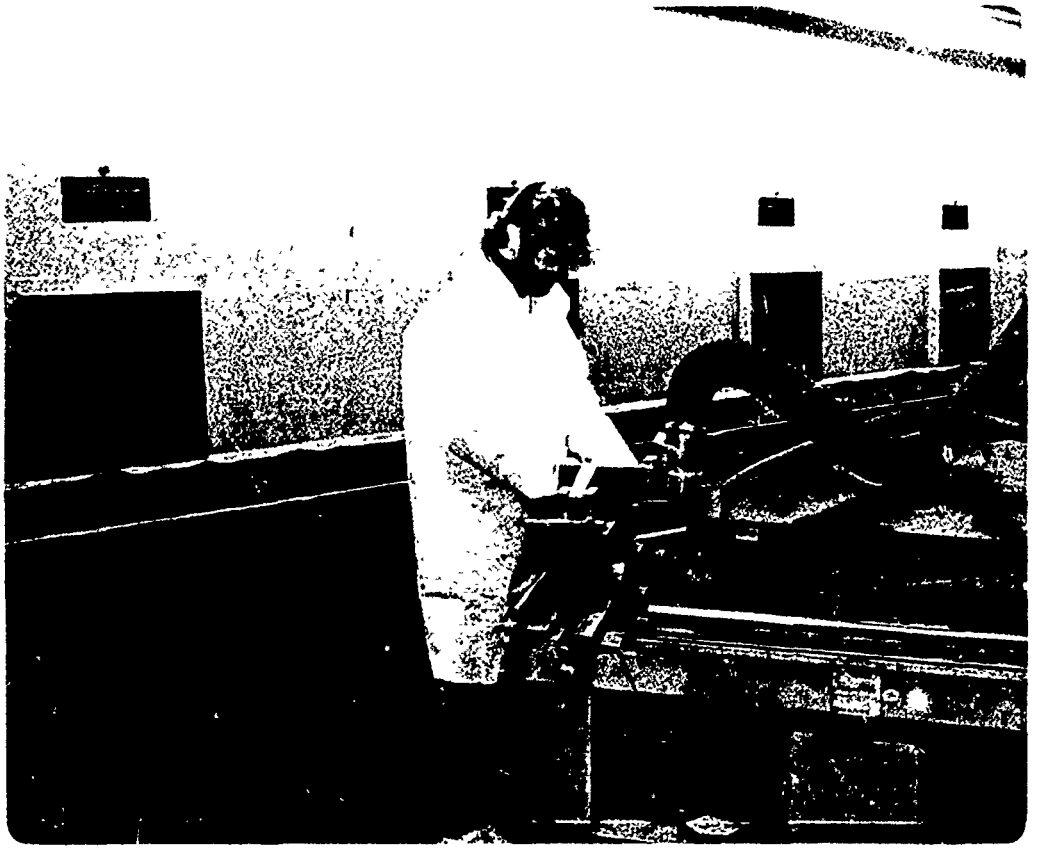


Figure 18. Sawing graphite/epoxy vertical stabilizer skin.

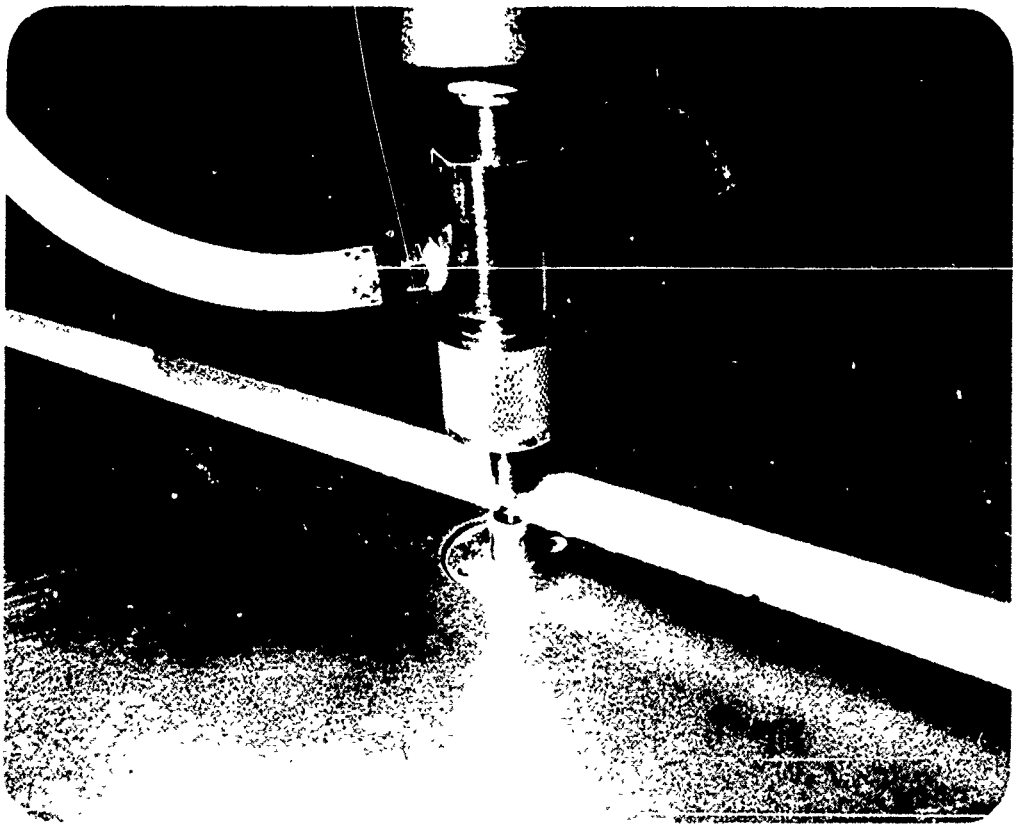


Figure 19. Abrasive water-jet stream cutting fiberglass/epoxy rod.

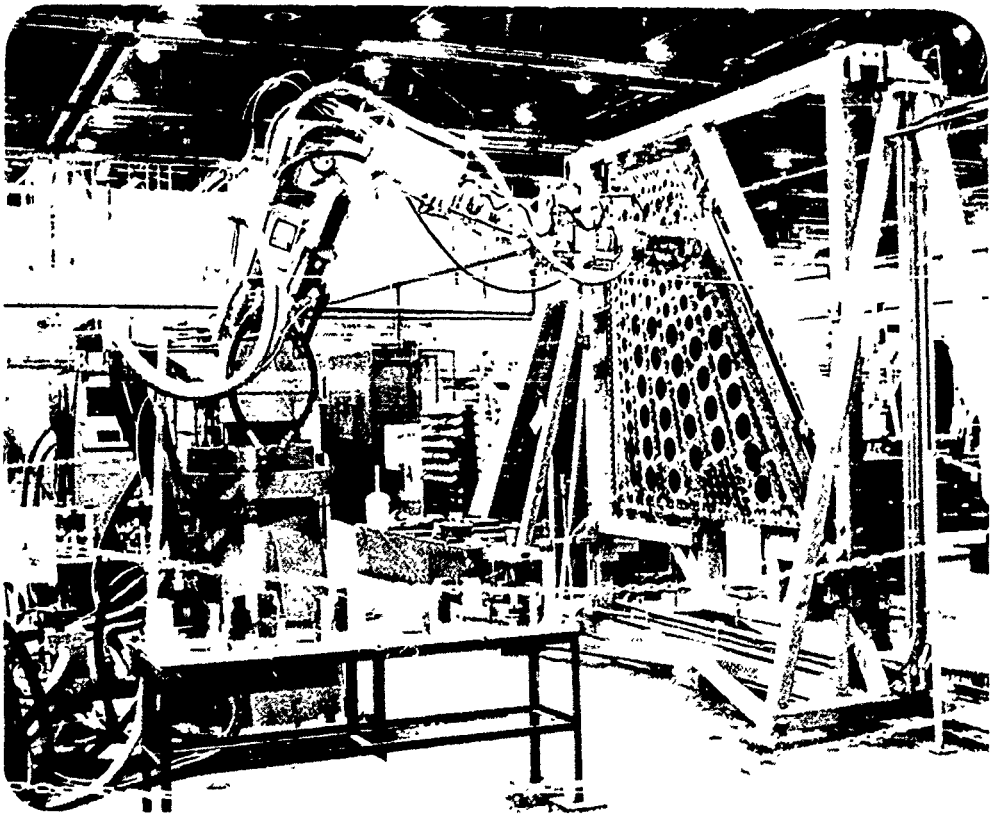


Figure 20. Robotic drilling station for graphite/epoxy horizontal stabilizer skin.

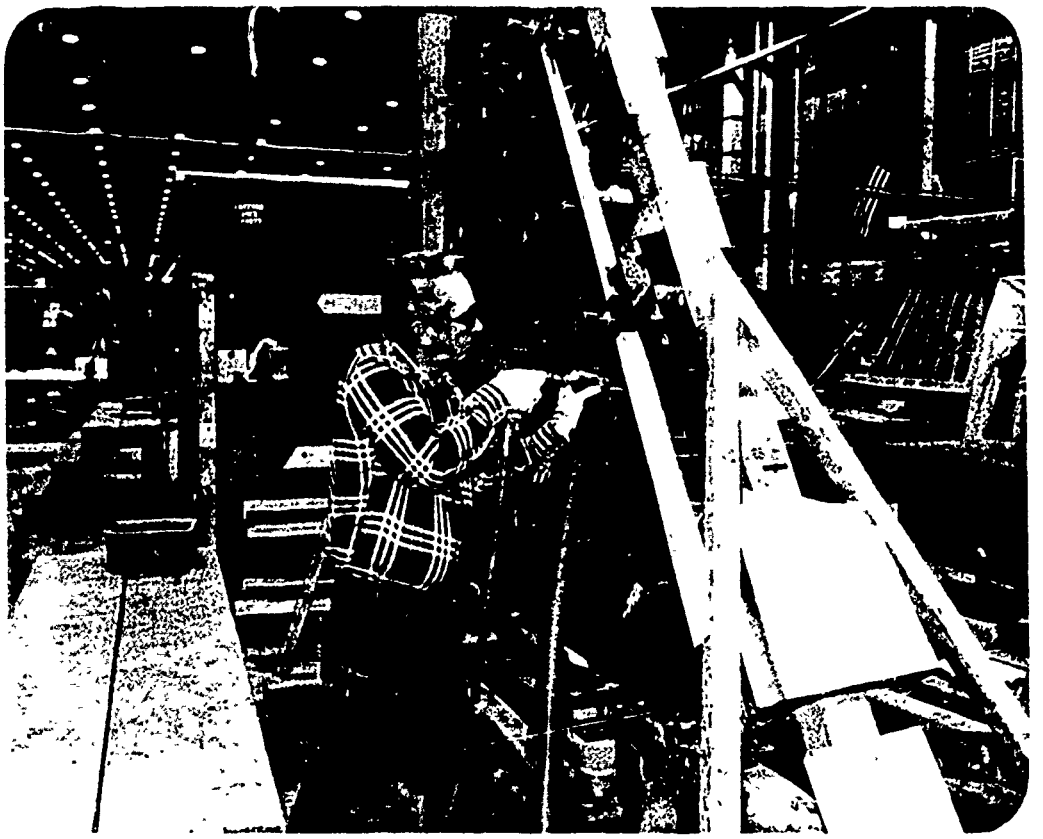


Figure 21. Manual drilling of a graphite/epoxy horizontal stabilizer skin.

automated robotic drilling of composites. Manual drilling is used to supplement the robotic drilling. A vacuum is used to remove drill shavings as they are produced in both automated and manual drill operations. The composite shavings are collected dry, bagged, and sent to approved land fills. After the drilling process is complete, the manufacturing procedure for composites parallels that of sheet metal fabrication in producing a flyaway part (Fig. 22).

ACKNOWLEDGMENTS

The author would like to thank Mr. J.R. Brooks - Manager of Bonding and Composites Fab., Mr. W.L. Vineyard - General Foreman of Composites Fab. and Mr. T.F. Campbell - Industrial Hygienist for their support.

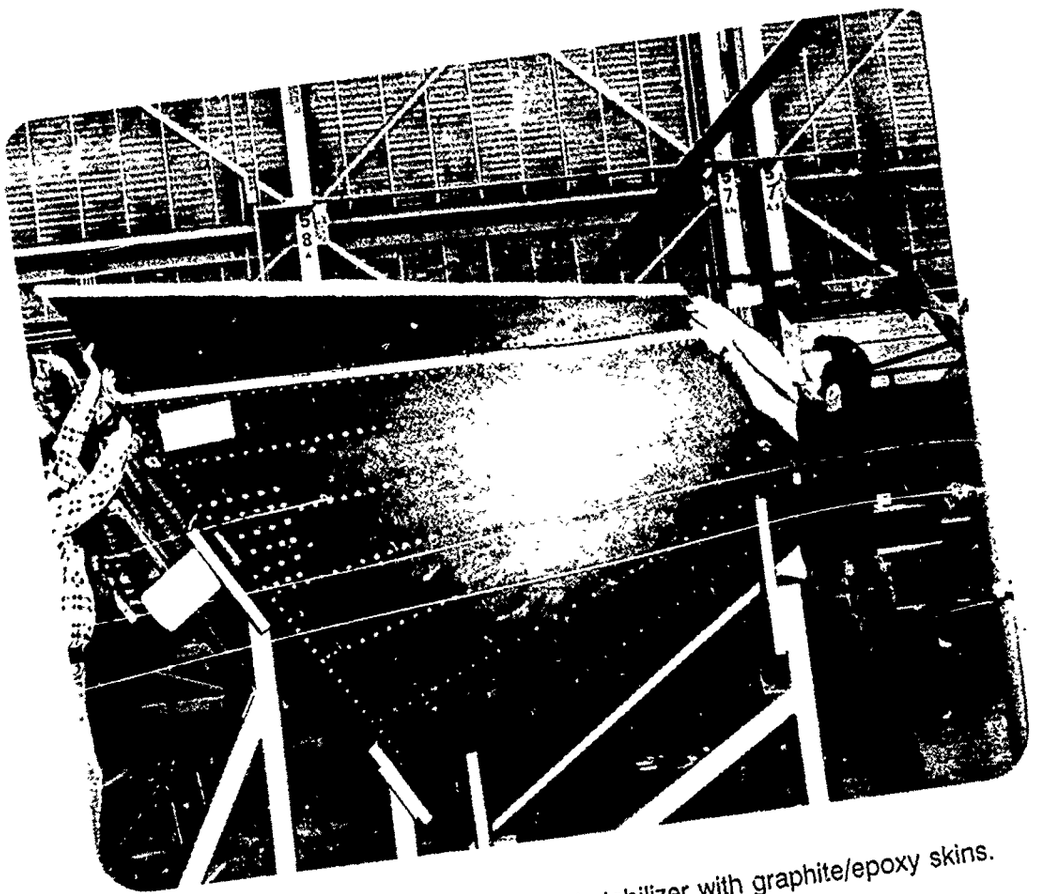


Figure 22. Assembled F-16 horizontal stabilizer with graphite/epoxy skins.

INTRODUCTION TO SUPPORTABILITY OF ADVANCED COMPOSITES

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ABSTRACT

Supportability of advanced composite structures is a tremendously broad subject. It includes everything from the basic design concept of the structure, to the specific materials used to manufacture it, how that particular structure meshes with other composite structures in the weapon system as a whole, and the training, technical data, repair methods, personnel and support equipment required to keep that structure functional. This paper is meant to familiarize those unacquainted with advanced composites with some basic supportability requirements of advanced composite repair.

BACKGROUND

Advanced composites were first introduced to aircraft in the early 1970's (see Fig. 1). Boron fibers (boron vapor-deposited onto a tungsten filament) with an epoxy matrix were used to construct the horizontal stabilizers for the Navy's F-14. The Air Force was also soon in the composite business with boron/epoxy horizontal stabilizers on the F-15. All other advanced composite structures since then (except for the B-1 longeron) have been made of graphite/epoxy due to the expense and difficulty when working with boron fibers.

The Air Force has only three fixed-wing weapon systems presently flying with appreciable amounts of advanced composite structures: The F-15, the F-16, and the recently introduced B-1B. The composites on these aircraft are limited to secondary structure, mainly in the flight control surfaces and tail section. In addition to these aircraft, in-house programs by the Air Force have retrofitted the A-10, F-111, C-130, and C-141 with a number of advanced composite structures. The Navy also has three fixed-wing aircraft with composite structures: the F-14, F-18, and AV-8B. The F-18 and AV-8B have a much higher percentage of their structural weight constructed from advanced composites than any previous weapon system; the Navy, therefore, has the greatest amount of composite repair experience.

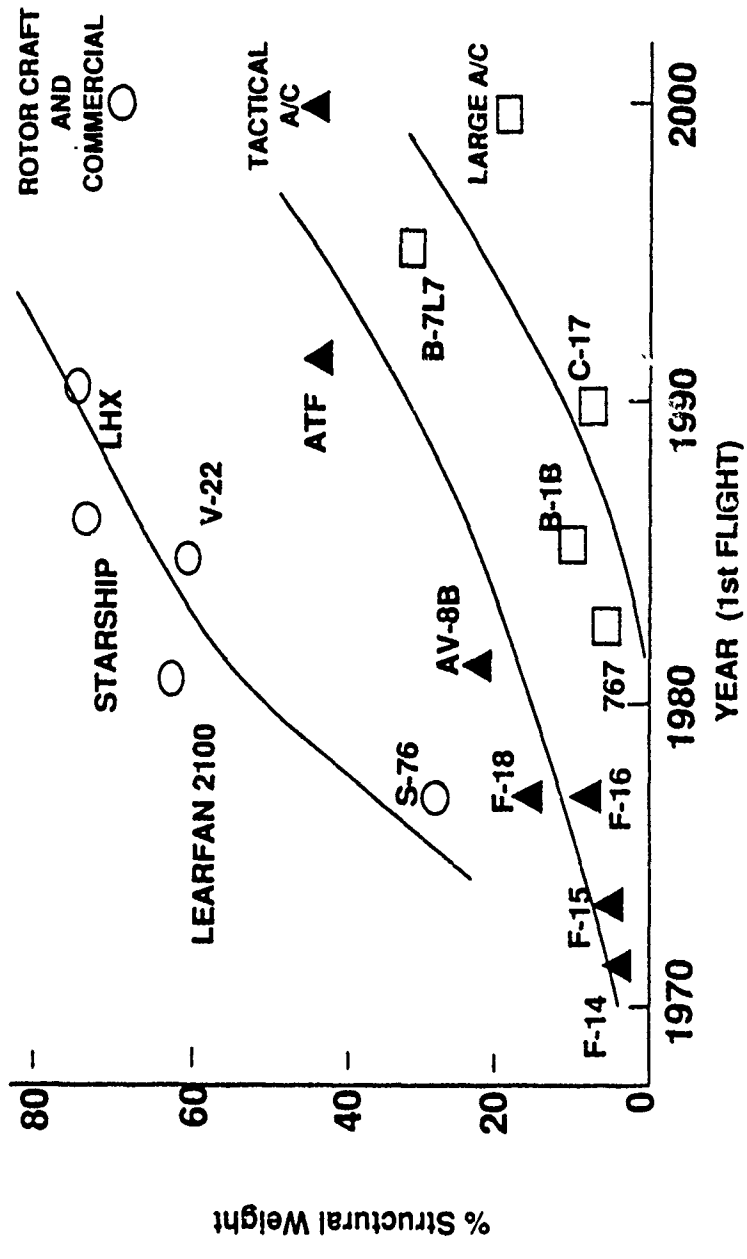


Figure 1. Current and projected advanced composites usage on aircraft.

The next 5 years will see a dramatic increase in the amount of composites used in active DoD aircraft. The Air Force will be receiving the C-17, V-22, B-2, and the Advanced Tactical Fighter (ATF). The Navy will add the V-22 and the A-12 (the Advanced Tactical Aircraft or ATA) to the fleet. These new aircraft will have up to 60 percent of their structural weight in the form of advanced composite structure, and additional structure made from conventional composite materials such as fiberglass. It is evident that advanced composites will become a significant part of the aircraft's supportability requirements.

AIR FORCE DEPOT ASSIGNMENTS

Within the Air Force, Air Force Logistics Command (AFLC) is assigned the responsibility of supporting a weapon system once it is through the acquisition phase. AFLC has five Air Logistics Centers (ALCs), each with responsibility for specific weapon systems. The following is a list of the weapon systems with advanced composites and which ALC provides support:

- Oklahoma City ALC (OC-ALC)/Tinker AFB, OK
  B-1 B-2
- Ogden ALC (OO-ALC)/Hill AFB, UT
  F-16 Air Launched Cruise Missile
- Sacramento ALC (SM-ALC)/McClellan AFB, CA
  A-10 F-111 ATF
- San Antonio ALC (SA-ALC)/Kelly AFB, TX
  C-17
- Warner-Robins ALC (WR-ALC)/Robins AFB, GA
  F-15 C-130 C-141 V-22

The experience base across the depots varies due to their workload. WR-ALC and OO-ALC currently repair the F-15 and F-16, respectively. OC-ALC is preparing itself for the B-1. SA-ALC has a Military Construction Project planned for 1992 to build a facility to handle the composites on the C-17. They are also working with the Air Force Advanced Composites Program Office (ACPO), located at SM-ALC, to redesign and fabricate various T-38 structures. SM-ALC presently has only one advanced composite structure that was provided by an airframe contractor; the underwing pivot fairing on the F-111. The ACPO has

redesigned the F-111 forward strake and A-10 leading edges into advanced composite structures; these structures are now being produced in-house by SM-ALC.

LEVELS OF REPAIR

One of the key elements to supportable advanced composite structures are the repair techniques. Different techniques are used for different levels of repair. Aircraft Battle Damage Repair (ABDR) scenarios put severe constraints on the amount of time a repair may take (8 hours) and the potential environment that will exist (forward operating location, possibly contaminated by chemical/biological agents). Field-level repairs may take place on the aircraft. It is common, however, for structures to be removed and replaced at the field level since this usually allows the aircraft to be available sooner. The repair can then take place in the local shop or be sent back to the depot. In the depot-level repair environment the repair is not performed under the time constraints that are present in ABDR or field-level repair conditions. Depots also have the facilities, equipment, and engineering support to perform large area repairs.

NON-DESTRUCTIVE INSPECTION

Before the repair can begin, the damaged area must be identified. This is not as easy with composites as it is with metal structures. Typical damage such as a low velocity impact (e g., a dropped tool) would cause a dent in metals; however, the stiffness of the advanced composite fibers causes them to spring back to their original position, leaving no visible surface damage. Looks are deceiving, because delamination within the laminate may have occurred, and the composite skin may have debonded from a supporting honeycomb core (see Fig. 2). The easiest way to locate damage of this type is to tap the surface with a special hammer (although a quarter is acceptable and readily available). Any dull sound will indicate a debond or delamination.

Ultrasonic inspection equipment is a quantitative means of locating damage in the composite structure. This equipment ranges from small, portable devices that may be used on the aircraft to large fixed systems used in the depots. X-ray equipment may be helpful for locating defects in the skin or core.

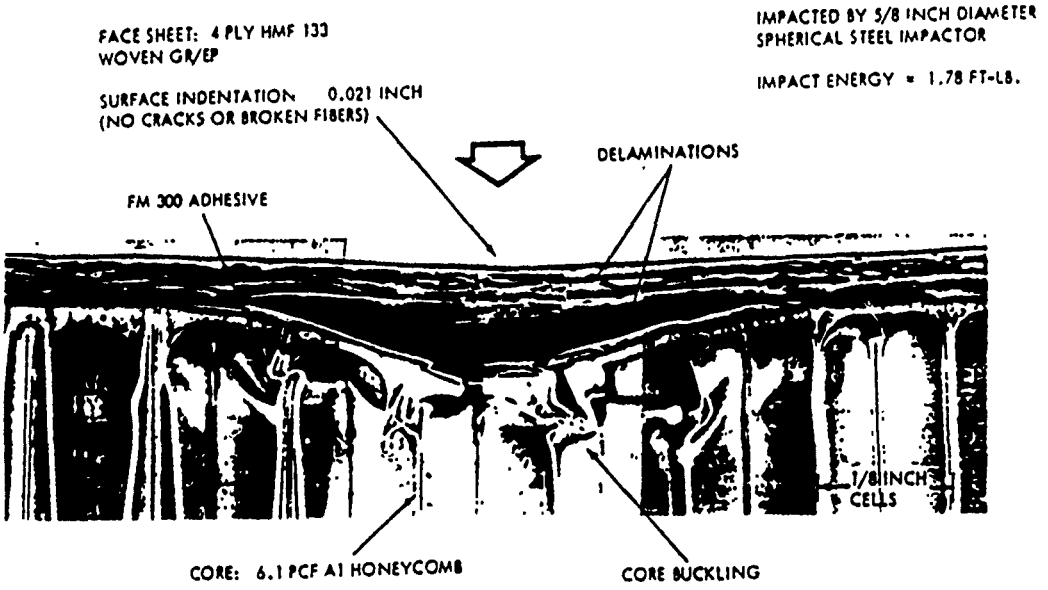


Figure 2. Impact damage on a composite skin with honeycomb core.

PAINT REMOVAL

Having located the damage, steps can now be taken to repair the composite structure. Before the repair can take place, the paint from the repair area must be removed. The amount of paint removed and the removal technique will depend on the size of the repair and the equipment available. For a minor repair this may involve removing the paint from several square inches. A depot may remove the paint from the entire structure. Care must be taken with all the depainting techniques not to damage the composite substrate.

Chemical paint strippers have long been used to remove paint from metallic structures. Unfortunately, they are of limited use for composites because the chemicals used to strip the epoxy paint will also attack the composite's epoxy matrix. This will cause degradation of the composite's structural properties. In addition, the hazardous waste problems associated with chemical strippers make their use less attractive.

Hand sanding is the method of paint removal used for small-area repairs. Sanding is done either with a rotary sanding disk or a self-addressing flap wheel. Special care must be taken when sanding to take off paint only down to the primer. It is easy to be overzealous when removing the last specks of paint and take the first few plies of composite along with it.

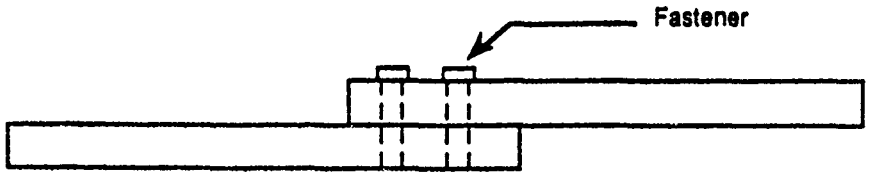
In the future, most large area paint removal in the Air Force will be done with Plastic Media Blast (PMB). The PMB technique uses beads of a given hardness to impinge on the painted surface. The kinetic energy and sharp edges of the beads chip the paint off. The hardness, size, application pressure, application angle, and standoff distance may all be varied to control the paint removal rated. In practice, PMB is usually done manually by a mechanic holding equipment similar to a fire hose. Maintaining the angle and standoff distance on contoured surfaces can be difficult, especially if the operator is fatigued.

The Air Force is also investigating the use of light energy for paint removal. Both the laser and the flash lamp use light energy to vaporize the paint off the substrate. The flash lamp is a pulsed Xenon arc lamp. The main difference between the flash lamp and a laser is that the laser generates coherent light. An early prototype of the flash lamp was tested at SM-ALC and showed promise; however, there is no funding available for further development. The laser is still in the laboratory development phase. Both systems show promise for the future.

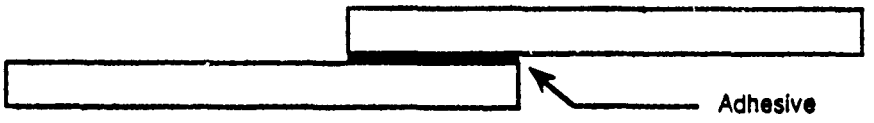
REPAIR TECHNIQUES

There are many methods of creating the joint between the parent laminate and the repair patch. There are two distinct classes of joints: bolted and bonded (see Fig. 3). The bolted repair is easier to perform, but the fastener holes significantly affect the parent laminate's strength and must be taken into account. Bonded repairs have better load transfer but require more support equipment and a higher skill level to perform. The patch itself may be made from many different materials:

- metal such as aluminum or titanium,
- procured composite patch,
- uncured preimpregnated composite plies (prepreg),
- wet layup.



Bolted Joint



Bonded Joint

Figure 3. Examples of bolted and bonded joints.

The choice of which type of joint and repair material to use is a function of the:

- time,
- tools,
- facilities,
- materials,
- skill level of the mechanics,
- technical data or engineering assistance,

available to perform the repair. The availability of these items limits the size of damage that can be repaired in the field. Depots, such as OO-ALC, have shown that they are capable of large area repairs, such as reskinning the horizontal stabilizer of the F-16.

The damaged area must be removed before a repair is performed. For minor surface damage, this may be as simple as light hand sanding with fine grit sandpaper; for more extensive damage, a router or power sander is used. Any damaged substructure must also be removed and replaced.

A scab patch (see Fig. 4) is the easiest repair to perform. The damaged area is cleaned up, and a patch is either bonded with adhesive or bolted with fasteners onto the parent laminate. The repair patch is typically either a metal patch or precured composite patch specially designed for that weapon system. The disadvantages of this type of patch are that the load transfer into the patch is eccentric and that it does not leave a smooth aerodynamic surface.

Step and scarf repairs (see Figs. 5 and 6) are repairs in which the damage is removed from the parent laminate in a tapered fashion and the repair patch is placed flush with the outer mold line of the skin. Scarf repairs can be considered step repairs with an infinite number of steps. These repairs are more difficult to perform than scab patches, but there is better load transfer through the repair. The repair patch can also match the parent laminate in the number and orientation of the repair plies. This can bring the laminate back to its original strength and stiffness. The repair also has the added advantage of leaving the structure with an aerodynamically smooth surface.

Finally, the repair technician also may choose applying a wet layup to the repair area. A wet layup consists of a laminating resin applied to a fabric (the fabric is commonly fiberglass, although it may be graphite or aramid). It is considered a low strength repair that would not bring the laminate back to full strength. This type of repair is useful for small areas (less than 1 inch diameter holes) or to fill a lightly loaded area for aerodynamic purposes.

SUPPORT EQUIPMENT AND FACILITIES

The equipment/facilities required to perform advanced composite repairs varies with the level and type of repair. Bonded repairs require more equipment and facilities to perform. Most structural adhesives/preimpregnated composite materials require storage at 0° F or below and have a limited shelf life. It is logistically difficult to keep a field unit supplied with small quantities of film adhesives or prepregs. They have only small freezers in which to store the materials and no laboratory facilities to update them at the end of their shelf life. These materials also require a temperature/humidity-controlled room to perform the repair layup. It is an added burden on the field unit to maintain a proper layup room.

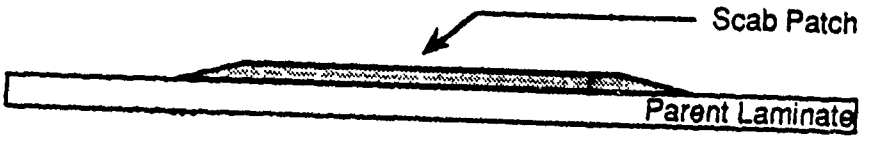


Figure 4. Scab patch.

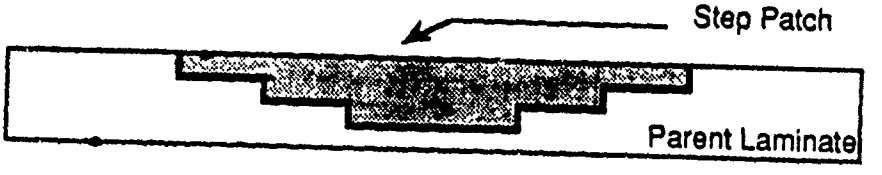


Figure 5. Step patch.

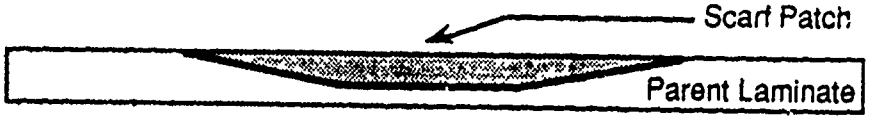


Figure 6. Scarf patch.

The adhesives/prepregs used in aerospace applications require heat and pressure to obtain a proper cure. Depots have large temperature/pressure vessels, called autoclaves, for curing their structures. Autoclaves are not practical at the field level, placing limitations on the size and type of repairs that can be done there. Heat and pressure for field repairs are provided by heat blankets and vacuum pumps. These have been packaged into portable units called "hotbonders." They are commercially available from several vendors.

Depaint is another area where depot and field equipment may vary. Air Force depots will be using PMB as their near-future method of large-scale paint removal. Component paint removal may be done by PMB or by sanding. PMB facilities are too expensive to place in each field unit. Sanding, therefore, will be their method of paint removal.

TECHNICAL DATA

The major sources of technical data for the repair of advanced composites are the specific weapon system technical orders (T.O.s) and the General Advanced Composite Repair Process Manual, T.O. 1-1-690. If damage exceeds the limits in the T.O., a structural engineer will have to design a repair for that specific structure. Major rework, such as the F-16 horizontal stabilizer reskin, would be done against the originals blueprint. A revision to T.O. 1-1-690 will be available this Spring along with a companion document, the Advanced Composites Repair Design Training Guide.

TRAINING

The Air Force has two in-house sources for training in advanced composites. Air Training Command offers two courses, one a traveling familiarization course and the other an intensive, hands-on course for military personnel. The ACPO offers a series of courses for both engineers and mechanics. These courses are open to anyone within the Department of Defense.

FUTURE

The future will hold many challenges for those involved in the supportability of advanced composite structures. New coatings for stealth technology will have to be stripped in order to perform the composite repair and then be reapplied. Increased aircraft performance will require matrices that can handle the increased temperature requirements

Epoxy-matrix composites handle today's airframe requirements. Bismaleimides and polyimides will be necessary to handle airframe and engine requirements of the ATF. A new class of thermoplastic matrices is beginning to mature and is certain to play a role in next generation aircraft. This will require a new way of performing repairs, and will greatly affect the overall supportability requirements of the composite structure.

MATERIAL TRENDS IN ADVANCED COMPOSITES

Diana Carlin

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ABSTRACT

Composite structures have become an integral part of many military systems. From their initial use on the F-14, F-15, and F-16, an extensive amount of research has been focused on understanding these unique materials and their processing. The Materials Laboratory at the Air Force Wright Aeronautical Laboratories has continually lead the development and characterization of advanced composites from initial research and development, through advanced development and manufacturing technology. The future of composite materials offers many unique opportunities for furthering the performance of composites.

As part of the Air Force's Project Forecast II, new technology efforts are being pursued to support the development of ultra-lightweight composite aircraft that are 50 percent lighter than current high performance aircraft. This will require a combination of new materials technologies, with the principal focus being on high performance reinforcing fibers. New, ultra-high tensile strength carbon fibers offer great promise, but improvements will be needed in their compressive properties to fully realize their potential. Ordered polymer fibers and films have demonstrated low density, high tensile strength and high modulus. Molecular composite technology offers the potential for creating a tough, self-reinforced composite that could greatly simplify future manufacturing techniques.

MATERIAL TRENDS

I'd like to present a historical perspective of composite materials and then move into what you can expect in the next 20 years.

I will be addressing material trends so that we can learn from our experience in the past and apply that to the future. The first chart represents the theme of the presentation: Advanced Composite Evolution. We started back in the early sixties looking at initial materials development. The reason composite materials are of interest is the specific strength and specific stiffness (material property divided by the density). You notice in the lower left-hand corner of the chart the traditional metal materials are shown including

aluminum, titanium, and steel. Composites offer a significant increase in both strength and stiffness over these materials. Conventional materials such as AS4 carbon fibers and epoxy fall into approximately this area. New materials that I will be discussing during this lecture increase both strength and stiffness. The ultimate goal is to find a balance in properties.

Composites offer many other advantages over conventional metals. It is possible to form very complex shaped parts which may require drilling and a series of different processes to be manufactured with metals. We may also take advantage of the tailorability of composite materials to form conductive and non-conductive materials. Composites offer increased fatigue and corrosion resistance. For space applications, composites offer controlled thermal expansion, as well as dimensional stability. Lower acquisition costs become possible by incorporating automated fabrication. We can reduce the number of parts in the aircraft structure, thereby reducing assembly costs. We are also looking at lower life cycle costs because of reduced supportability requirements.

Building on this initial materials development, we began looking at advanced materials development, including feasibility and weight savings. Composite materials started to be applied in a very limited way to early military aircraft including the F-14, the F-15, the F-16. Graphite reinforced epoxy was used in these early aircraft. From this initial production experience, we started looking ahead to determine how we can better develop, manufacture and support composite materials.

The F-15 has approximately 2 percent of its structural weight comprised of composite material. The F-18 is approximately 10 percent by weight, and the AV-8B, which is 27 percent by weight composite materials. It is projected that for future advanced systems over 40 percent of the structural materials will be composite. As we move into the late 1980's and 1990's, composite research has begun to investigate controlled manufacturing. We are looking at on-line quality assurance techniques, as well as in-process controls, and expert systems.

Let's go back to basics for just a minute to remind you of the basic constituents of a composite: the fiber and the matrix. There is also a very important interphase where the fiber and matrix come together. These three areas are the individual components of the composite equation. I will be focusing on the fiber and matrix specifically as I discuss the future trends of these materials.

The military's experience with carbon fibers has traditionally focused on PAN based fibers. These fibers provide high strengths and strain-to-failure, but have been limited by their moduli. Pitch-based fiber, on the other hand, demonstrates very high modulus with intermediate strengths. We are starting to develop new organic fibers. These fibers can provide very high modulus and low density. They are also tailorable to give excellent electrical properties and dimensional stability. There are also inorganic materials which are being investigated such as silicon carbide. These have a very high temperature capability, as well as excellent electrical properties.

I'll now discuss the second half of the composites equation: the matrix. We have heard a lot about epoxy materials this morning. They are considered the workhorse of composite matrices. They are currently flying on several aircraft and thousands of pounds of preimpregnated product forms are used each year. There are several limitations with epoxy materials. They tend to have relatively low use temperatures and are brittle. Advanced materials that we are looking at include bismaleimides. Originally these materials were more brittle than epoxy. A lot of work has gone on in the past five years or so in toughening the bismaleimides (BMI) material. The BMIs are similar to the epoxies in processing. They require a cure cycle (heat and pressure cycle) to chemically react the resin system. BMIs also require a postcure which increases the overall process cycle time. Thermoplastic matrices are very different from epoxies and BMIs. There is no tack or drape associated with these materials, due to the fact that the resin is fully reacted in the prepreg. Thermoplastics do offer a wide range of use temperatures. Thermoplastics also offer the advantage of low manufacturing cost potential, which we are currently investigating.

Future research areas will include the translation of high performance fiber properties into composite properties, new high temperature matrix materials and novel processing approaches.

The BMIs offer several advantages over standard epoxies: we can get 350° Fahrenheit hot-wet performance, they are processed similar to the epoxies, and they are commercially available. The disadvantages associated with these materials include toughness, reproducibility, and intermediate modulus fiber compatibility.

Thermoplastic matrices are chemically different than the thermosetting material. These systems are not chemically cross-linked as are the thermosetting matrices. Also, they are fully reacted when impregnated on the fibers. Therefore, what a prime aerospace

manufacturer would receive in the shop is a fully reacted chemical resin system. We are now taking the chemistry away from the aircraft manufacturers and leaving it to the resin manufacturers. One distinct advantage of thermoplastics is that reforming is possible. By applying heat and pressure, it is possible to reform the part within the constraints of the fibers. Because thermoplastics are fully chemically reacted, there is no out time limitation with these materials. Refrigerated storage is not required. There is a reduced amount of moisture absorption with thermoplastic materials versus an epoxy resin. This is important for several reasons: it is important in space applications (low condensibles) and it is very important for repair applications.

Thermoplastics also offer several other advantages: they are inherently tougher than epoxies and bismaleimides. In the laboratory we have demonstrated up to ten times toughness on a coupon scale and in structural components about two to three times the toughness of a standard epoxy. This gives us better structural efficiency and also greater damage resistance. We also have improved processability. As I mentioned before, you do not have to cure this material once it comes into your shop, so you no longer have to go into an autoclave for an eight- or ten-hour cure cycle and then a four- or five-hour post-cure. The material is already chemically reacted; you simply place it in a press or use some way to get energy into it, use heat and pressure to form the part and you have a completed part. If something happens during the process cycle, if you lose pressure or if your heat cycle fails or something like that, you put it back in the tool and do it again. This leads to a low acquisition cost part. By using metals-forming techniques, which are very rapid, to form parts that would take eight or ten hours in an autoclave, we are able to reduce cycle time, reduce bagging requirements, etc. We also have improved supportability with thermoplastics. Because of the increased toughness, one would expect to have reduced repair frequency Reprocessing is possible if you have not damaged the fibers to an extent where they can no longer carry the load. So, if someone simply dented the top of the material due to a tool drop or delaminated an edge due to a drop, simple repairs are possible.

Currently there are several components made of thermoplastic composites that are on operational aircraft. These include the C-130 bellyskin and several access panels and doors We are also gathering repair experience, and battle damage information from these components. We are hoping that all the experience that we have gained in the past five years will feed into advanced fighters and transport technology.

Now, as we look even further ahead, research is trying to increase the performance of composite materials. The following figures illustrate that we are currently stretching the theoretical limits of fibers and the matrices (see Figs. 1-3). Beyond this, how can we, how do we make composites that are tougher and more damage tolerant? How can we improve the fibers by improved processing or orientation? How do we improve the matrices? And then how do we incorporate all these improvements into a design? We are trying to emphasize designing a part to take advantage of composite properties. All of this increased performance feeds into what is called ultra-lightweight structures. As was mentioned earlier with Project Forecast II, with ultra-lightweight structures the ultimate goal is to gain a 50 percent weight savings over state-of-the-art aircraft. We are looking at several different aspects of ultra-lightweights structures in the Materials Lab and also in industry. The ultra-lightweight materials and structures program encompasses several different disciplines; it is not just making materials better. It includes advanced fibers and polymers, but it also includes different metals techniques. It includes advanced design concepts and integrating the materials and the design. It also includes advanced manufacturing.

Several new developments which we foresee in the next ten or twenty years include ordered polymers and molecular composites. We are currently working on those in the laboratory. Ordered polymers can be oriented into two different material forms; fiber and film. The properties of ordered polymers far exceed what we are seeing in current materials technology today. We are seeing an increase in mechanical properties and we are also seeing a tailorability in the optical and electrical properties which is very important. The ordered polymers technology again plays a major role in the Project Forecast II. It will be incorporated into the ultra-lightweight structures. We will be looking at nonlinear optics and trying to integrate all of this into the ultra-lightweight program. Molecular composites is another subset of ordered polymers technology. Molecular composites are rigid rod reinforced materials. The reinforcement actually comes on the molecular level. Mechanical properties are very exciting in the preliminary phase. Again, molecular composites will feed into Project Forecast II and ultra-lightweight materials.

This is a graphical representation of conventional composites vs. a molecular composite (see Fig. 4). In a conventional composite you have a fiber that is your reinforcement with a diameter of five to ten microns. A molecular composite has its reinforcement at the molecular level on the order of a few angstroms. So you are looking at

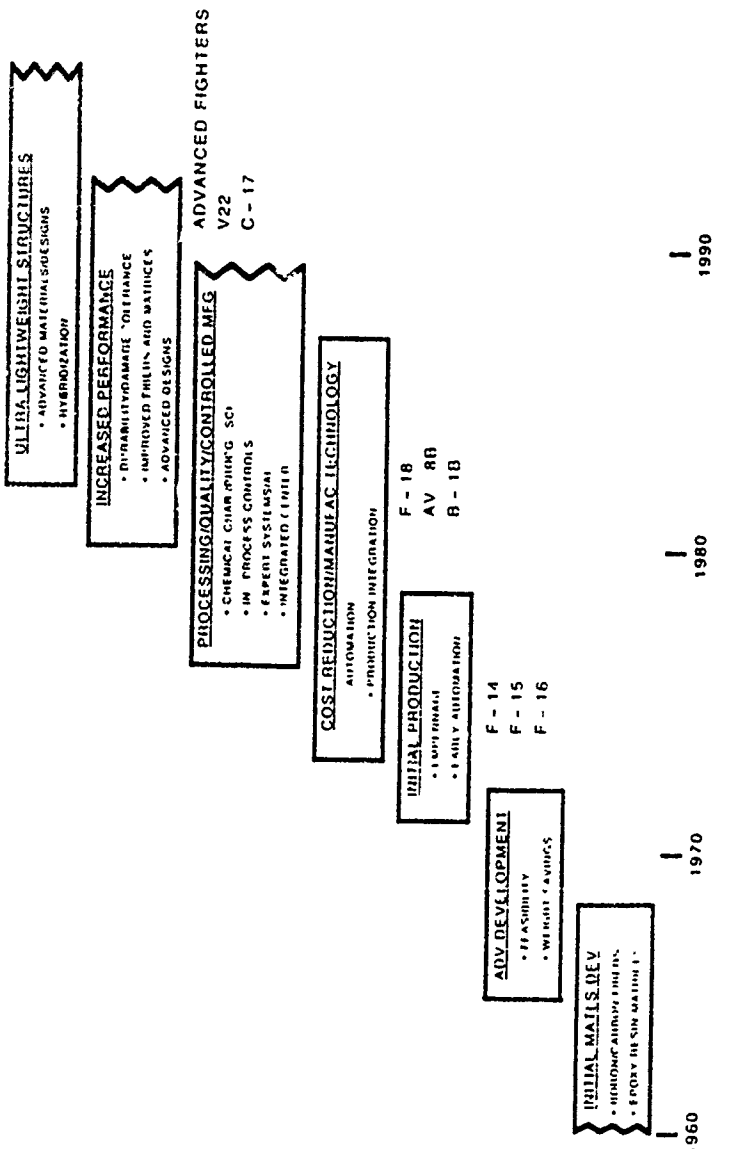

Figure 1. Advanced composites evolution.

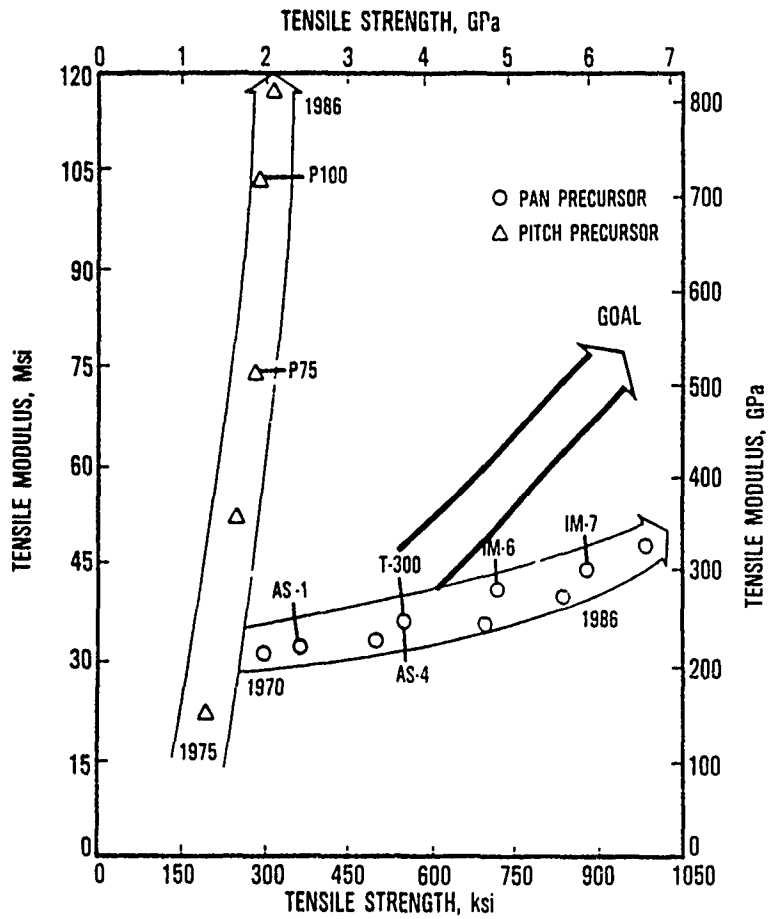

Figure 2. Aerospace carbon fibers trends in structural properties.

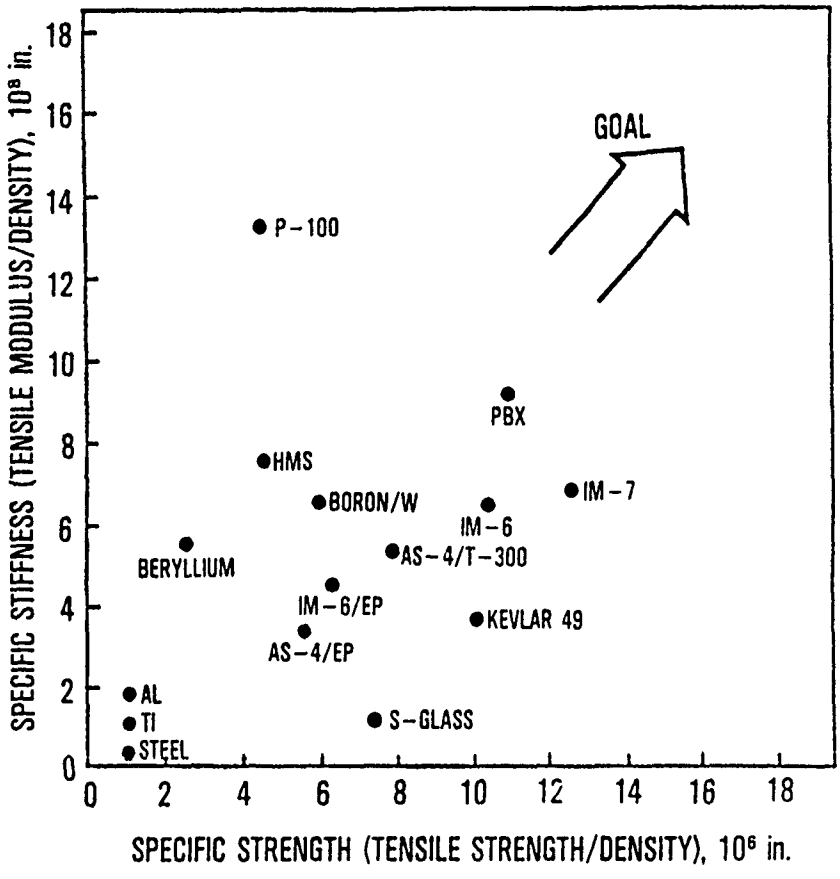

Figure 3. Comparative properties of advanced materials.

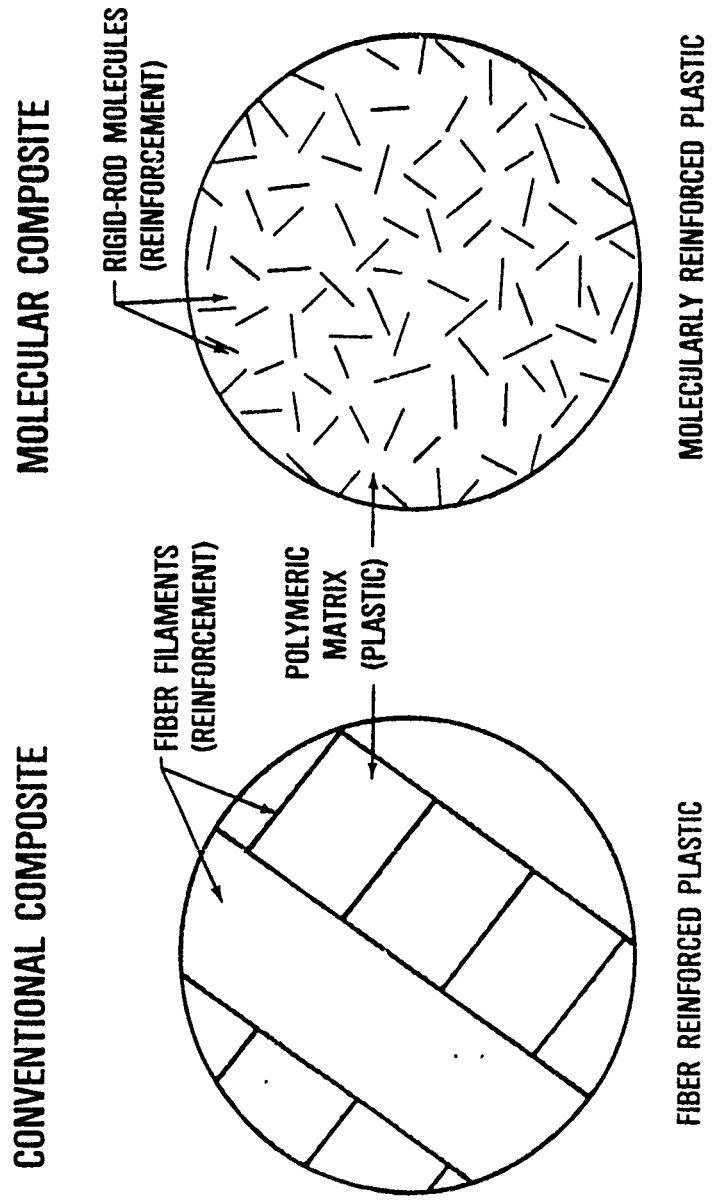

Figure 4. Molecular composites concept.

very similar polymeric matrices that can be thermoset or a thermoplastic material but we are looking at very unique and exciting rigid rod molecules to provide the reinforcement. We would foresee that the processing of these materials would be very similar to what you would see today. If it was a thermosetting matrix you could use several different processes for rolling or extruding a pseudo-prepreg material and then do classical processing on it to come up with your final part. Now, if a thermoplastic matrix was used we could form standard sheets stock and have that simply lying around and then when the part is needed you could simply form the part to shape.

In conclusion, we followed the materials trends all the way from back in the early sixties through what we see will be occurring up into the year 2000.

IV. HEALTH EFFECTS AND EXPOSURE CONSIDERATIONS

CONSENSUS STATEMENT

The toxicology and industrial hygiene issues associated with advanced composite components and matrices are those of complex mixtures. These health issues aren't unique to the advanced composite industry. Intelligent assessments of human health hazards of complex chemical mixtures are made, despite the paucity of data on such mixtures, throughout the chemical industry. These hazard assessments are made by integrating information on the inherent toxicity of the various components in such complex mixtures with data on exposure to the mixture.

Because of the rapid evolution and turnaround of resin matrix systems and toxicological studies requiring years, evaluation of individual resin systems isn't feasible Rather, the hazards associated with individual components of a given resin matrix system have been and should continue to be evaluated. The individual component data should be combined into an averaged hazard assessment. Such an assessment is based on known effects of these components and sound scientific judgment. The establishment of exposure standards for complex mixtures will be dependent on validation of current techniques and models of exposure.

Polymer matrix resin systems are chemically diverse and reactive systems by design Therefore, the uncured materials present a variety of potential health hazards The degree and scope of the hazard is dependent on the particular resin system used.

Exposures to mixtures of gases, vapors, and liquids, as well as man-made fibers and particles, are possible during various composite operations.

Approximately one half of composite matrix systems contain epoxy based resins Most forms of unreacted epoxy resins have a low order of acute toxicity and aren't readily absorbed. Epoxy resins may produce skin irritation or sensitization

Other resin systems of importance include the polyurethanes and urea- and phenol-formaldehyde resins (U/F and P/F). The isocyanate component of uncured urethane resins and formaldehyde in the U/F and P/F resins present hazards to the worker both in terms of acute toxicity and potential chronic effects. In addition, the minor additives must be considered since many are skin irritants and sensitizers and may be potentially carcinogenic

or teratogenic. Precautionary action should be taken to avoid all skin contact with uncured resin systems. Owing to their sticky nature, resins on the skin are difficult to remove, and workers shouldn't use solvents to remove them because they facilitate skin penetration of the resin systems. In general, most unreacted resin systems may also cause eye and respiratory irritation

Relative to raw fiber production, numerous studies on carbon, graphite, fiber glass, and aramid fibers have indicated that in general, most reinforcement fibers have diameters outside the respirable range. Those which are respirable have low airborne concentrations and low order of toxicity permitting their use in composite manufacturing operations without undue health risk to workers. Exposure to reinforcement fibers may cause mechanical irritation of the eyes, nose, and throat.

Composite dust is primarily composed of cured binder with relatively low concentrations of free fibers. Preliminary studies indicate these dust are capable of producing lung insult greater than "nuisance dust" but far less than quartz dust Therefore, treating these dust as "nuisance dust" may be inappropriate In general, cured resin dust from composite reworking may cause eye and respiratory irritation.

In certain cases, monitoring techniques can be employed to measure exposure to composites materials. Surface contamination testing, biological monitoring, and product analysis all produce information which may be useful in a hazard assessment

In developing recommended exposure limits, factors to be considered include 1) identification of the material, contaminant, or decomposition product causing the adverse health effect; 2) type of work, processes used, and demographic characteristics 3) quantitative personal exposure measurements; and 4) the health outcome being studied and its time relationships with the presumed harmful exposure

RECOMMENDATIONS

Since some fibers can absorb contaminant chemicals, future studies should assess this situation along with the pyrolysis products of composite matrices

Future research in these areas of development and use of innovative monitoring methods, worker health surveillance, toxicity testing, and chemical dermal penetration measurements will provide useful information to health professionals performing composite material exposure evaluations

A specific national defining criteria for the hazards associated with composite components should be established. The American National Standards Institute (ANSI) publishes a standard entitled "American National Standards Guide for Classifying and Labeling Epoxy Products According to their Hazards Potentiality". The intent of this standard is to provide producers and distributors of epoxy resins and related products with classification criteria and labeling recommendations so they can better define the hazard categories into which their specific products fall and design labels that will warn the buyer and user of any hazards that exist. The resin system additives aren't specifically covered in the scope of the ANSI guide; however, the same criteria for assignment can be used to rate them on a comparable basis.

TOXICITY OF ADVANCED COMPOSITE MATRIX MATERIALS

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ABSTRACT

As we enter an age where advanced composite materials appear to be making significant inroads in many new applications, the dilemma facing many health professionals is the need to be able to make intelligent assessments of human health hazards despite having extremely limited toxicity information, if any at all, on the formulated resin matrix. With the rapidly evolving nature of these matrices, and the costs associated with comprehensive toxicity testing, one is forced to examine the hazards associated with the components of a given resin system and perform a weighted-average hazards assessment, based on known effects of the systems components and sound scientific judgement. This paper highlights the toxicity of a few of the more important components.

Perhaps half of all advanced composite resin systems are epoxy resin-based. The most widely used epoxy resins found in current advanced composites are those based on diglycidyl ether of bisphenol A. DGEBPA is not particularly toxic but, like most epoxy resins, is a skin and eye irritant and a potential dermal sensitizer. Long-term feeding and skin painting studies with DGEBPA have indicated little, if any, carcinogenic potential.

Methylene dianiline and sulfonyl dianiline are the major aromatic amine curing agents used in epoxy resin systems. Both have been shown to cause cancer in animals, but extrapolation of these findings to man is questionable. Other resin systems of importance include the polyurethanes and urea- and phenol-formaldehyde types. The isocyanate component of uncured urethane resins (e.g., toluene diisocyanate) and formaldehyde in the U/F and P/F resins present hazards to the worker both in terms of acute toxicity (skin and eye irritants; sensitizers) and chronic effects (both linked with development of cancer in animals).

Other types of resin systems, PMR 15, bismaleimides, polycyanurates (triazines), thermoplastics, etc., are briefly reviewed, and mention is made of the hazards of several solvents used in advanced composite-materials processing.

INTRODUCTION

When this Conference was first planned, it was to have been an informal get-together of 15 or 20 people interested in the field of advanced composite toxicity and health hazards. The charter of that group was to have been a discussion of the issues of health and safety of advanced composite materials. Needless to say, the breadth and depth of the meeting have grown significantly. This growth has come with the realization that we now stand on the threshold of a rapidly expanding phase of finding advanced composites in many new areas of use. These uses are not only those with military and aeronautical applications but, just as important (if not more so for the formulators and manufacturers), we are seeing the birth of private, commercial applications of advanced composites on a large scale (for more detail on the emerging applications of advanced composites, see papers presented in Section III of these Proceedings: Composite Technology Overview).

One of the problems currently facing this industry is that with the rapid growth in the use of these materials, exposure of the composites to workers and private consumers will also grow rapidly. At the same time this is happening, we as health professionals are still wrestling with the problems of looking at health hazards of the composites, as they are used

Table 1 presents a general outline of the strategy often used in the development of toxicologic data for a given chemical (for further detail, see, for example, Chan et al., 1982, and Stevens and Gallo, 1982). Once there is sufficient commercial interest in a chemical to warrant study, the toxicologist will initiate some simple acute studies: oral, dermal and, perhaps, inhalation LD_{50}s; eye and primary dermal irritation studies; dermal sensitization; mutagenicity. As interest in the chemical grows, and potential for exposure expands, subchronic studies (14 to 90-day) by appropriate routes of exposure are considered Such studies look for effects from repeated dosing, and may be especially useful in identification of target organs. Finally, for selected chemicals to which many persons are expected to be exposed, chronic, two-year or lifetime studies may be conducted. These detailed and often extremely expensive studies are usually designed to look for whole-life effects and carcinogenesis. Other studies looking at reproductive effects, etc., are conducted as is considered necessary. This entire process for a given chemical might take seven to ten years, but will provide the investigator with a good idea of the effects of the chemical in animals. Then, the quantum leap of faith - extrapolation to man - is made.

TABLE 1

Example Strategy for Development of Toxicity Data

Acute Studies (1 - 2 weeks) ($4,000 - 5,000)	• LD_{50} (oral, dermal, other) • Irritation (skin, eye) • Sensitization (allergic reaction) • Mutagenicity (Ames, etc.)
Sub-chronic Studies (2 weeks - 3 months) ($50,000 - 100,000)	• Expected route of exposure • Effects from repeat exposure • Target organ effects • Reproductive effects, teratology
Chronic Studies (18 mo - 2 yr; lifetime) ($250,000 - 2,500,000)	• Expected route of exposure • Effects of long-term exposure • Target organ effect • Carcinogenicity

Editorial Comment:

Few, if any, matrix systems can support the costs associated with a full, chronic toxicology program.

In the area of advanced composites, however, the resin matrix formulae, that part of the composite which gives each manufacturer's product its unique properties for the specific application, change quite rapidly in an ever-evolving manner. As a result of this, by the time subchronic or chronic testing would be completed, the resin system may no longer be of commercial interest. This fact, coupled with the economic burden of extensive toxicity testing and the reality of the business world, has given rise to the current state-of-the-art in hazard assessment used by the advanced composite industry. Often the resin formulator will not have done any studies on a given, blended resin system. Instead, the toxicologist will carefully examine the known toxicity/hazards of the individual materials that are in the system These data, coupled with sound, scientific judgement, allow the hazard evaluator to conduct a weighted-average hazard assessment for the mix.

In early 1987, the Suppliers of Advanced Composite Materials Association (SACMA), convened a task force[a] to look into this situation. The group was asked to examine the manner in which health hazards in the industry are assessed, and prepare a briefing paper for the industry on the topic. Probably the only easy task the group had was to discover that all of the companies represented, which constitute a substantial portion of the advanced composite market share, look at their resin matrices as complex mixtures and judge the hazard of the mixture as described above. The task force was unable to identify any manufacturer that looks at the subchronic or, especially, chronic effects of formulated resin systems in any sort of systematic manner. Rather, the industry norm is to rely on the manufacturers of the monomers, hardeners, fillers and other formulation components to provide sufficient information upon which a hazard assessment can be made.

One final comment by way of introduction is appropriate. It is important for anyone dealing with advanced composites, or any other chemical for that matter, to keep in mind that "All chemicals are toxic, there is none which is not The right dose differentiates a poison and a remedy". This axiom is drawn from the 16th-century writings of Paracelsus, the Father of Toxicology.

Toxicology has been defined as the science that investigates the adverse systemic effects of chemicals (Ottoboni, 1984). Hazard, on the other hand, integrates exposure of a chemical with this inherent toxicity:

(TOXICITY) x (EXPOSURE) = HAZARD.

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[a]The author wishes to acknowledge the efforts of all members of SACMA's "White Paper Task Force" for allowing me to draw liberally from what has been a group effort in writing. Task force members included: Charles Schwartz (Hercules Incorporated, the current Task Force Chairman), Thomas Confer (BASF/NARMCO; initial Chairman), Alan Taylor and Janos Schulze (CIBA-Geigy Corporation), Mel Kantz (Ferro Corporation), Donald Cross (Hexcel), Lori Falkner and Jennifer Heth (ICI Composites Inc./Fiberite), and Glen Morehead (Shell Oil Company). This document is expected to be available through SACMA (Arlington, VA) in late spring 1989.

In certain instances, a chemical may be quite toxic[b] but, if precautions are taken to limit exposure, little hazard[b] may be present. Consider, for example, the toxicity of botulinum toxin or cyanide. People are, for the most part, acutely aware of the toxic nature of these chemicals and, therefore, few people are exposed to them. As a result, the overall hazard associated with these chemicals is minimal. (Of course, they remain extremely toxic and hazardous to those who are exposed to them.) The converse may also be true. Extreme overexposure to a relatively non-toxic material can cause anoxia and excessive urination, damage to the lungs and kidneys, and can be fatal by certain routes of exposure under extreme conditions; however, most people don't think about water in this light!

The balance of this paper presents highlights of the available toxicity information for some of the major resin monomers presently used in the matrices of advanced composite materials. I have not provided significant detail nor have I attempted to cover the entire spectrum of materials currently in use. Rather, I have selected some of the more important resins and monomers in the hope of presenting an overview of broadest utility.

Among the most common matrix materials currently in use are the epoxy resin-based formulae, representing perhaps 50 percent of the total market. Nearly all the epoxy resins are manufactured by making a central core or backbone, and then reacting epichlorohydrin with it to give it its functionality. The pendant "epi" group is chemically known as a "glycidyl" group and, hence, the epoxy resins are often chemically named as glycidyl ethers, diglycidyl ethers, glycidyl esters, glycidyl amines, etc. Residual epichlorohydrin in these resins is often measurable, and ranges from a few ppb to a percent or so. Resins commonly used domestically have typical residual epichlorohydrin levels in the 1-10 ppm range (Morehead, G. T., Shell Chemical Company, Houston, TX, personal communication).

Residual epichlorohydrin (see Structure I) in epoxy resins may be of concern because epichlorohydrin is known to cause irritation of the eyes, skin and respiratory tract, and to be a dermal sensitizer (Shell, 1983 and 1986). Epichlorohydrin has also been shown to cause

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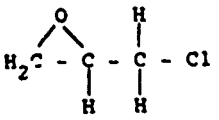
[b]In the context of most U. S. regulatory agencies' activities, these terms are used in a slightly different manner. In many regulatory documents, HAZARD is considered to be the inherently harmful effect of a chemical while RISK is the likelihood that this hazard may be expressed in an individual. The reader is cautioned that the established, basic definitions of toxicity and hazard are used throughout this document.

STRUCTURE I

EPICHLOROHYDRIN (Epi, ECH)



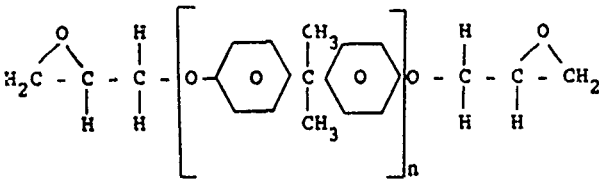
- Animal: Irritant, Sensitizer (?)
  Reversible Sterility
  Carcinogen (IARC; ACGIH,...)
- Human: Irritant, Sensitizer, Clastogen
  No epidemiologic link to cancer

chromosomal changes in humans (Kucerova et al., 1976; Sram et al., 1980; White, 1980), though no link to human cancer has been demonstrated (Enterline, 1982; Tassignon et al., 1983). In animals, epichlorohydrin is toxic, extremely irritating and absorbed by all routes of exposure (Shell, 1983; see also references in: Hine et al., 1982). It may be a sensitizer and has also caused reversible sterility in animals. No similar testicular dysfunction has been reported in humans (Milby, 1981). Based on positive evidence of carcinogenesis in animals via multiple routes of exposure, the International Agency for Research on Cancer (IARC) has classified epichlorohydrin as a probable human carcinogen (Group 2A; IARC, 1987). It is also classified by NTP as a substance that may reasonably be anticipated to be carcinogens (Group B; NTP, 1985). One should, again, be reminded of the difference between toxicity and hazard. With residual epichlorohydrin levels in the ppm-or-less range it is quite unlikely that these toxic effects would be encountered by workers protected properly and trained in the correct methods to handle resin systems and prepregs safety.

The workhorses of the advanced composite epoxy resins are those based on the reaction of bisphenol A (or bisphenol A oligomers) and epichlorohydrin (DGEBPA; see Structure II). These bisphenol A epoxy resins have been shown to be practically non-toxic and only slightly irritating (for a summary review of the literature, see Shell, 1984). They may, however, be skin sensitizers and, as for any industrial chemical, direct contact should be kept to a minimum. Because of their widespread use, the diglycidyl ether/bisphenol A resins are one of the few matrix components that have been extensively studied.

STRUCTURE II

DIGLYCIDYL ETHER OF BISPHENOL A (DGEBPA)



- Skin painting studies: Oak Ridge National Labs
  Shell Research Labs
- IARC: Insufficient evidence to classify (in press)

Holland et al. (1981) have reported that a solution of DGEBPA painted on the skin of mice daily for two years caused no effect on the animals' body weight or hematological or clinical chemistry parameters of either sex. There were no treatment-related tumors observed, although chronic, local inflammation was seen, indicating that a maximum tolerated dose (MTD) was achieved. In addition to this 2-year skin-painting study, a 26-week feeding study in rats at 0.2 to 5 percent bisphenol A resin in the diet has also been reported (Hine et al., 1958). All animals receiving 5 percent test material died, but there were no deaths or significant lesions at 0.2 percent.

Zakova et al. (1985) have reported that repeated (two-year) epidermal application of a technical grade of DGEBPA did not have any effect on survival in CF1 mice, nor was there any excess in either skin or systemic tumors over vehicle (acetone-treated) controls. Another recent report also examined the carcinogenic potential of DGEBPA (Peristianis et al., 1988). In this study, while tumors of the skin and subcutis (the connective tissue beneath the skin) were noted in several treated animals, both at the site of application as well as at remote, untreated sites, the incidence of such tumors was not statistically significant when compared to concurrent vehicle (acetone-treated) controls. Peristianis et al. (1988) did comment, however, that if the incidence of skin tumors seen in these animals were to be compared to historical controls in their lab, the data could be interpreted to indicate that at least two of the test materials (pure DGEBPA and a technical DGEBPA with a residual epichlorohydrin < 3 ppm) might have exhibited a low order of carcinogenic potential to the skin of this particular

strain of mouse (CF1). Although some increases in numbers of systemic tumors were also observed, the authors did not feel that they were indicative of a biologically significant response. Finally, neither the incidence nor severity of non-neoplastic, background pathology were influenced by treatment with any of the three materials in this study.

Although not yet published, IARC has recently reviewed the data on DGEBPA and decided that there was insufficient information to classify its carcinogenic potential (Group 3; this IARC monograph (Volume 47: Organic Solvents, Some Resin Monomers, Some Pigments, and Occupational Exposures in the Painting Trades) is due to be published July, 1989).

None of the epoxy resin monomers has an established TLV or OSHA PEL (ACGIH, 1988-89; OSHA, 1989). Epichlorohydrin has a TLV of 2 ppm with a "skin" designation (ACGIH, 1988-89). In the recent Federal Register announcement of OSHA's updated Air Contaminant Levels (OSHA, 1989), epichlorohydrin is designated to have a PEL of 2 ppm and a skin designation.

Other epoxy resins besides diglycidyl ether of bisphenol A have been more or less well studied (for review, see Hine et al., 1982). Perhaps one of the most comprehensive series of systematic studies conducted have been those done by Benjamin van Duuren et al and published through the '60s and early '70s, primarily in the Journal of the National Cancer Institute (van Duuren, 1969; van Duuren et al., 1963, 1965, 1966a, 1966b, 1967a, 1967b, 1971, 1974). Other seminal papers include those by Hine et al. (1958), Weil et al. (1963) and Manson (1980).

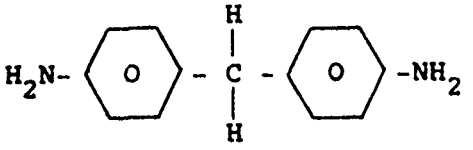
Used in conjunction with the epoxy resins are hardeners and curing agents, mostly amines, amides or anhydrides. Perhaps two of the most widely used, and also the most well studied, are the aromatic amines, methylenedianiline (MDA, Structure III) and 4,4'-sulfonyldianiline (diamino diphenylsulfone; 4,4'-DDS, Structure IV).

Methylenedianiline currently has a TLV of 0.1 ppm - skin and is classified as a suspect human carcinogen, A2 (ACGIH, 1988-89). It is also designated as a possible human carcinogen by IARC (2B; IARC, 1986a).

It has been reported that chronic exposure of rats to the dihydrochloride salt of methylenedianiline has caused liver and kidney injury (Lamb et al., 1986). Indeed, MDA has long been recognized as being capable of causing liver damage (jaundice) in humans following oral or dermal exposures (Kopelman et al., 1966). Based on the finding of thyroid

STRUCTURE III

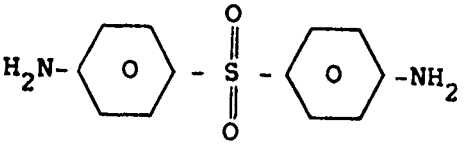
METHYLENEDIANILINE (MDA)



- Liver, kidney injury (Epping Jaundice)
- Liver, thyroid tumors (NTP; rats/mice, male/female)
- Urinary bladder tumors (NIOSH; questionable study)
- NO CONFIRMED MDA-RELATED CANCERS IN MAN

STRUCTURE IV

4,4'-SULFONYLDIANILINE (DIAMINO DIPHENYLDULFONE; DDS; DAPSONE)



- NCI Study - spleen and connective tissue tumors.
- Metabolized differently in mouse/man.
- Dapsone - drug of choice for treatment of leprosy for decades.

and liver tumors in both sexes of rats and mice, NTP has recently judged MDA to be a carcinogen (NTP, 1986). A single epidemiological study of MDA-exposed workers at a helicopter plant outside Philadelphia has turned up an excess number of bladder tumors (NIOSH, 1983). An extremely limited number of workers were involved in the study, however,

making the statistical treatment of the data suspect. To date, there have been no confirmed reports of MDA-related cancer in man.

As previously mentioned, another commonly used epoxy hardener is 4,4'-sulfonyldianiline. 4,4'-DDS has been reported by the National Cancer Institute to cause tumors of the spleen, and osseous metaplasia (growth of bone tissue) in the spleen and abdominal connective tissue (NCI, 1977). NCI speculated in their report of the bioassay that these tumors would not be seen in humans due to differences in the way rats and humans metabolize the compound (NCI, 1977). This is further supported, considering that a pharmaceutical preparation of 4,4'-DDS, dapsone (Jacobus Pharmaceutical Company, Inc.), has been the treatment of choice for leprosy and certain types of chronic dermal inflammation since the 1940s. In this treatment regimen, dapsone is taken orally at 300 mg/kg daily for a lifetime (such an extended treatment is necessary since dapsone is a bacteriostat, not a bactericide; Mandell and Sande, 1980). IARC has judged that the data on dapsone are currently insufficient to allow any classification (Group 3; IARC, 1987)
Other types of hardeners and curing agents include the aliphatic and cycloaliphatic amines, amides, and anhydrides. Representative members of each of these classes are categorized as irritants, though some, such as the amides, are noticeably less irritating than the others. As with much of the other chemistry related to advanced composites, many of these other types of hardeners may cause an allergic reaction in dermally-exposed individuals Some of the hydrophthalic anhydrides have relatively high vapor pressures at processing/curing temperatures, and the vapors generated may be irritating to the skin, eyes and respiratory tract. Respiratory sensitization (an allergic, asthmatic-type reaction) is also reported following exposure to anhydride curatives.

Although epoxy resin-based systems currently make up, perhaps, 50-75 percent of the advanced composites market, with bisphenol A-type resins accountable for approximately one-half of that share, some of the other, smaller-volume and correspondingly less-well-studied types of matrices should also be examined.

The next major type of matrix system to be discussed is the urea-formaldehyde (U/F) and phenol-formaldehyde (P/F)-type resins. At present, these resins are of great interest in the industry due to problems associated with exposure at several aerospace manufacturers' facilities. (These events are the topic of several other papers in these Proceedings and will not be discussed at present.) The acute toxicities of U/F and P/F resins are fairly low. These

resins are irritants especially to the eyes and respiratory tract and, due to the presence of free formaldehyde, may cause skin sensitization.

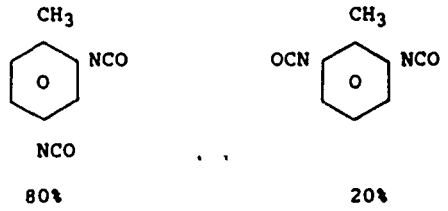
A brief review of recent developments in the study of formaldehyde toxicity has recently been published (Greenblatt, 1987). Formaldehyde is a fairly strong skin sensitizer. Many of the preservatives and biocides used in cosmetics, and shown to be sensitizers, work through the in situ release of formaldehyde. Sensitization reactions in the workplace are not uncommon. For example, textile finishing applications result in a substantial number of cases of occupational allergic dermatitis each year. Along with these dermal reactions, there is an association between formaldehyde and decreased pulmonary function, although such findings vary widely.

In the early 1980s, CIIT (Chemical Industries Institute of Toxicology) and New York University independently published the results of studies which indicated that high levels of formaldehyde caused the development of nasal cancers in rats (Swenberg et al., 1980; Albert et al., 1982). In contrast, in 1986 the National Cancer Institute and the Formaldehyde Institute (NCI/FI) jointly published the results of a retrospective epidemiological study of some 26,000-plus workers, employed in 10 formaldehyde-producing or -using facilities going back into the 1940s (Blair et al., 1986). The NCI/FI data indicated that there was no relationship between cancer rate and occupational formaldehyde exposure in humans. That finding by NCI/FI has received much attention and is disputed by many others looking at the same data set (see discussions in: Nelson et al., 1986). For the purposes of these Proceedings, I think it might be safest to say that the jury is still out on the risk for humans exposed to formaldehyde. Currently, formaldehyde has a TLV/PEL of 1 ppm (ACGIH, 1988-89; OSHA 1987). It is designated as a suspect human carcinogen by ACGIH (A2; ACGIH, 1988-89), a probable human carcinogen by IARC (2A; IARC, 1987), and among those substances that may reasonably be anticipated to be carcinogens by NTP (b; NTP, 1985).

Of the other types of matrices currently found in advanced composites, among the most important are the polyurethanes. In this category, the toxic species is usually not the polyol precursor, but the cross-linking agent, the diisocyanate By far the most important of these is toluene diisocyanate (TDI; Structure V), although methylene diisocyanate (MDA) and hexamethylene diisocyanate (HDI) are also used.

STRUCTURE V

TOLUENE DIISOCYANATE (MIXTURE OF 2,4- AND 2,6-ISOMERS)



- Respiratory Sensitizers
- Animal Carcinogen (NTP; IARC)

Perhaps the most unique aspect of diisocyanate toxicity is the generic association with respiratory sensitization (see the discussion of TDI in: ACGIH, 1988). Once this reaction appears in an individual exposed to, say, TDI, even exposure to extremely low airborne concentrations, a few hundredths of a part per million, may cause serious respiratory problems. Among the diisocyanates, there is also evidence of cross-sensitization, in which one is sensitized to one isocyanate but reacts to others, as well.

Based on a much-maligned NTP bioassay[c] (NTP, 1982), NTP has proposed to include TDI on its list of chemicals reasonably anticipated to be carcinogens (Group b in the NTP rating system; NTP, 1986). IARC felt in 1979 that the carcinogenic data on TDI were insufficient for classification (Group 3; IARC, 1986), but has since reclassified TDI as a possible human carcinogen (Group 2B). This reclassification is based on what they perceive as sufficient animal data, but no human data (IARC, 1986).

Another important resin currently in use is PMR-15 resin. This resin was developed by NASA and is licensed to several manufacturers for use in high-temperature, structural applications. Although little toxicological information is available for PMR-15, it is generally

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[c]The NTP study of TDI has been criticized for its choice of route of administration, lack of characterization of the test substance in the body, high test doses used, and experimental procedure discrepancies. In addition, experiments with rats and mice exposed to 0.05 or 0.15 ppm of the compound by inhalation, the most appropriate route of administration, for 6 hours per day, 5 days per week for two years did not confirm the NTP study findings (Loeser, 1983).

assumed that the major hazard involved in manufacturing and using PMR-15 composites is due to dermal exposure to methylenedianiline, one of the co-reactants in the uncured, or green, material. (The toxicology of MDA has been discussed above.) MDA is also found as a residual monomer in bismaleimide (BMI) resins prior to free-radical cross-linking of the BMI resin with other vinyl compounds.

Specific effects of long-term exposure to PMR-15 and BMI resins (also referred to as polyimides or simply imides) are not well characterized. They may cause irritation or sensitization upon prolonged and repeated contact and, as one might expect, dust and vapors generated during heating operations may cause eye or respiratory irritation.

Another newly-emerging type of matrix material is the polycyanate or triazine resin (Shimp, 1986). Little information is available about the long-term effects of these materials and, therefore, there is not much that can be discussed here.

The final types of matrix materials to be mentioned are the thermoplastics. These include a vast variety of materials, many of which are well studied but, as one might imagine, others that are not so (for reviews, see: Various Contributors, 1982). For the most part, thermoplastics appear to present little hazard except when they are handled in molten form Severe thermal burns may result upon contact with these molten materials. If the molten plastic comes in contact with the skin, one should be sure to run the exposed area under cold water to cool it, and then seek medical attention before removing the solidified plastic - simply peeling it off is likely to take the top layers of skin right off with it!

Obviously, there are many more chemicals that could be included here. Elsewhere in these Proceedings, there are discussions of the more important reinforcing materials, so they have not been mentioned here.

Another area that has been, as yet, completely avoided is that of the processing solvents used in advanced composite applications. These solvents include ketones such as acetone, methyl ethyl ketone (MEK) and methyl iso-butyl ketone (MiBK). These three are all mild-to-moderate skin irritants. Perhaps the most important health hazard associated with these ketone solvents is that of central nervous system depression following severe inhalation overexposure. (For an overview of ketone solvent toxicity, see Krasavage et al , 1982) Of course, the greatest hazard with the ketone solvents is probably that of flammability, a discussion of which is beyond the scope of this review.

To avoid the flammability issue, many manufacturers have replaced the ketones with chlorinated hydrocarbon solvents, such as methylene chloride, methyl chloroform, trichlorethylene, etc., in many applications. Some of these have been linked with development of cancers in laboratory animals and, based on these data, estimates of human risk have been developed. (A detailed discussion of the controversial use of mouse liver tumors as an indicator of human health risk will not be presented here.)

Some of the other types of solvents used in the advanced composites field include the various alcohols, glycol ethers (several of which are associated with male reproductive hazard; see Smith, 1984), dimethylformamide (DMF) and N-methylpyrrolidone. DMF exposure has recently been linked with the development of testicular cancer in humans, but this is another extremely controversial matter, and the facts are not at all clear at present (Levin et al., 1987; Chen and Kennedy, 1988).

As one might well imagine, the job of the toxicologist in assessing hazard associated with the binder systems and advanced composite materials is certainly a challenging one. In many cases this must be accomplished without much data, if any at all, for a given matrix system. Instead, the hazard assessor must rely on data for component parts of the system. That, in turn, is often scanty or controversial and conflicting.

It is hoped that through the joint efforts of the suppliers, the users and military, who, at present, are probably the largest "consumer" segment for much of the new technology, that we can all keep abreast of new developments in the field and continue to provide the worker with state-of-the-art health and safety information while our engineers and chemists produce state-of-the-art technology.

REFERENCES

ACGIH (1988) Documentation of the Threshold Limit Values and Biological Exposure Indices, Fifth Edition. American Conference of Governmental Industrial Hygienists. Cincinnati, OH.

ACGIH (1988-89) TLVs. Threshold Limit Values and Biological Exposure Indices for 1988-1989. American Conference of Governmental Industrial Hygienists. Cincinnati, OH.

Albert, R. E., et al. (1982) Nasal cancer in the rat induced by gaseous formaldehyde and hydrogen chloride. J. Natl. Cancer Inst. 68:597-603.

Blair et al. (1986) Mortality among industrial workers exposed to formaldehyde. J Nat. Cancer Institute 76:1071-1084.

Chan, P. K., et al. (1982) Principles and methods for acute and subchronic toxicity. in: Principles and Methods of Toxicology (A. Wallace Hayes, ed.) pp. 1-51. Raven Press, NY.

Chen, J L., and Kennedy, G L. (1988) Dimethylformamide and testicular cancer Lancet iss. 8575-6 p. 55.

Enterline, P. E. (1982) Importance of sequential exposure in the production of epichlorohydrin and isopropanol. Ann. N. Y. Acad. Sci. 381:344-349.

Greenblatt, M. (1987) Formaldehyde toxicology: A review of recent developments. Proc. Int. Cong. Role Formaldehyde Biol. Syst, 2nd. pp. 53-59.

Hine, C. H , et al. (1958) The toxicology of epoxy resins Arch Ind. Health 17:129-144.

Hine, C., et al. (1982) Epoxy compounds. in: Patty's Industrial Hygiene and Toxicology, Vol. 2A. (G. D. Clayton and F. E. Clayton, eds.). pp.2141-2258. John Wiley & Sons. NY, NY. (Information specific for DGEBPA is reviewed on pp. 2242-2247.)

Holland, J. M., et al. (1981) Chronic dermal toxicity of epoxy resins. I. Skin carcinogenic potency and general toxicity. Oak Ridge National Laboratory ORNL 5762 Special.

Holland, J. M., et al. (1987) Test of carcinogenicity in mouse skin: Methylenedianiline, q-glycidyloxytrimethyloxysilane, -aminopropyltriethoxysilane and a mixture of m-phenylenediamine, methylenedianiline and diglycidylether of bisphenol-A Oak Ridge National Laboratory. ORNL/TM-10472.

IARC (1979) Toluene diisocynate. in: IARC Monographs on the Evaluation of Carcinogenic Risk to Humans. Some monomers, plastics, synthetic elastomers and acrolein. pp. 303-340 WHO, IARC. Lyon, France.

IARC (1986a) 4,4'-Methylenedianiline and its dihydrochloride in: IARC Monographs on the Evaluation of Carcinogenic Risk to Humans. Some chemicals used in plastics and elastomers. pp. 347-368 WHO, IARC. Lyon, France.

IARC (1986b) Toluene diisocynate. in: IARC Monographs on the Evaluation of Carcinogenic Risk to Humans. Some chemicals used in plastics and elastomers. pp 287-324 WHO, IARC. Lyon, France.

IARC (1987) Epichlorohydrin. in: IARC Monographs on the Evaluation of Carcinogenic Risk to Humans, Supplement 7: Overall Evaluations of Carcinogenicity An updating of IARC Monographs Volumes 1 to 42. WHO, IARC. Lyon, France.

Krasavage, W. J., et al. (1982) Ketones. in: Patty's Industrial Hygiene and Toxicology, vol. IIC. (G. D Clayton and F. E. Clayton, eds.) pp. 4709-4800. John Wiley & Sons. NY, NY.

Kopelman et al. (1966) The Epping jaundice. Br. Med. J. 1:514-516.

Kucerova, M., et al. (1976) Mutagenic effect of epichlorohydrin, I. Testing of human lymphocytes in vitro in comparison with TEPA Mut. Res. 34:271-278.

Lamb, J. C., et al. (1986) Carcinogenesis studies of 4,4'-methylenedianiline dihydrochloride given in drinking water to F344/N rats and B6C3F1 mice. J. Toxicol. Environ. Health 18:325-337.

Levin, S. M., et al. (1987) Testicular cancer in leather tanners exposed to dimethylformamide. Lancet iss. 8568 p. 1153.

Loeser, E. (1983) Long-term toxicity and carcinogenicity studies with 2,4/2,6-toluene diisocyanate (80/20) in rats and mice. Toxicol. Lett. 15:71-81.

Mandell, G. L., and Sande, M. A. (1980) Antimicrobial agents (continued): Drugs used in the chemotherapy of tuberculosis and leprosy. in: Goodman and Gillman's The Pharmacological Basis of Therapeutics, 6th ed pp. 1214-1215 Macmillian Publishing Co., Inc. NY, NY.

Manson, M. M. (1980) Epoxides - is there a human health problem. Br J. Ind. Med 37:317-336.

Milby, T. H., et al. (1981) Testicular function among epichlorohydrin workers. Brit J Ind. Med. 38:372-377.

NCI (1977) Bioassay of Dapsone for possible carcinogenicity, CAS. No. 80-08-0 NCI-CG-TR-20.

Nelson, N., et al. (1986) Contribution of formaldehyde to respiratory cancer. Environ Health Perspec. 70:23-35.

NIOSH (1983) Health hazard evaluation report: Boeing Vertol Company. HETA 82-146-1366.

NTP (1982) NTP technical report on the carcinogenesis bioassay of toluene diisocyanate (86 percent 2,4-isomer and 14 percent 2,6-isomer) in F344/N rats and B6C3F1 mice (gavage study). NTP Technical Report 251.

NTP (1985) Fourth annual report on carcinogens, summary. NTP 85-002. U.S. Department of Health and Human Services, Public Health Service.

NTP (1986) National Toxicology Program; Carcinogins; Fifth annual report. Proposed rule. Fed. Reg. 51:35297-35298.

OSHA (1987) Occupational exposure to formaldehyde; Final rule. Fed. Reg. 52(233):46168-46312

OSHA (1989) Air contaminants; Final rule. Fed. Reg. 54(12):2329-2984

Ottoboni, M. A. (1984). The Dose Makes the Poison, p. 28. Vincente Books, Berkley CA.

Peristianis, G. C., et al. (1988) Two-year carcinogenicity study on three aromatic epoxy resins applied cutaneously to CF1 mice. Fd. Chem. Toxicol. 26(7):611-624.

Shell (1983) Epichlorohydrin health science and safety. Technical Bulletin SC:179-83 Shell Chemical Company, Houston TX.

Shell (1984) EPON/EPONOL/EPONEX Resins/EPON Curing agents Recommendations for Handling. Technical Bulletin SC:106-84. Shell Chemical Company, Houston TX.

Shell (1986) Epichlorohydrin safety data and information Technical Bulletin PI 3 1.1 Shell Industrial Chemicals, Houston, TX.

Shimp, D. A. (1986) The translation of dicyanate structure and cyclotrimerization efficiency to polycyanate properties. (Paper presented at the Spring Meeting of the American Chemical Society, New York. April 14, 1986).

Smith, R. L. (1984) Review of glycol ether and glycol ether ester solvents used in the coating industry. Environ. Health Perspec. 57:1-4. (It is suggested that the interested reader review this entire volume of Environmental Health Perspectives, vol. 57: Glycol Ethers.)

Sram, R. J., et al. (1980) Cytogenic analysis of peripheral lymphocytes in workers occupationally exposed to epichlorohydrin. Mut. Res. 70:115-120.

Stevens, K. R., and Gallo, M. A. (1982) Practical considerations in the conduct of chronic toxicity studies. in: Principles and Methods of Toxicology (A. Wallace Hayes, ed.) pp. 53-77. Raven Press, NY.

Swenberg, J. A., et al. (1980) Induction of squamous cell carcinoma of the rat nasal cavity by inhalation exposure to formaldehyde vapor. Cancer Res. 40:3398-3402.

Tassignon, J. P., et al. (1983) Mortality in an European cohort occupationally exposed to epichlorohydrin (ECH) Int. Arch. occup. environ. Health 51:325-336

van Duuren, B. L. (1969) Carcinogenic epoxides, lactones and haloethers and their mode of action. Ann. N. Y. Acad. Sci. 163:633-651.

van Duuren, B. L., et al. (1963) Carcinogenicity of epoxides, lactones and peroxy compounds. J. Natl. Cancer Inst. 31:41-55.

van Duuren, B L., et al. (1965) Carcinogenicity of epoxides, lactones and peroxy compounds, Part II. J. Natl. Cancer Inst. 35:707-717.

van Duuren, B. L., et al. (1966a) Carcinogenicity of epoxides, lactones and peroxy compounds. III. Biological activity and chemical reactivity. J. Med Chem 9:77-79

van Duuren, B. L., et al. (1966b) Carcinogenicity of epoxides, lactones and peroxy compounds. IV. Tumor response in epithelial and connective tissue in mice and rats J. Natl. Cancer Inst. 37:825-838.

van Duuren, B. L., et al. (1967a) Carcinogenicity of epoxides, lactones and peroxy compounds. V. Subcutaneous injection in rats. J. Natl. Cancer Inst. 39:1213-1216

van Duuren, B. L., et al. (1967b) Carcinogenicity of epoxides, lactones and peroxy compounds. VI. Structure and carcinogenic activity. J. Natl. Cancer Inst. 39:1217-1218.

van Duuren, B. L., et al. (1971) Carcinogenicity of isoters of epoxides and lactones: Aziridine ethanol, propane sultone and related compounds. J. Natl. Cancer Inst. 46:143-149.

van Duuren, B. L., et al. (1974) Carcinogenic activity of alkylating agents. J. Natl. Cancer Inst. 53:695-700.

Various Contributors (1982) in Patty's Industrial Hygiene and Toxicology (G. D Clayton and F. E. Clayton, eds.) John Wiley & Sons. NY, NY.

Weil, C. S., et al. (1963) Experimental carcinogenicity and acute toxicity of representative epoxides. Amer. Ind. Hyg. Assn. J. 24(4):305-325.

White, A. D. (1980) In vitro induction of SCE in human lymphocytes by epichlorohydrin with and without metabolic activation. Mut. Res. 78:171-176.

Zakova, N., et al. (1985) Evaluation of skin carcinogenicity of technical 2,2'-bis-(p-glycidyloxyphenyl)-propane in CF1 mice. Fd. Chem Toxicol. 23(12):1081-1089.

TOXICOLOGY OF CARBON FIBERS

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ABSTRACT

Carbon fibers are lightweight, high tensile strength synthetic fibers widely used for such commercial applications as sports equipment, reinforcing materials in structural composites, and prosthetic devices for humans. Carbon fiber can be synthesized from polyacrylonitrile (PAN) or from petroleum pitch. PAN-based fibers are the purer, more commonly used precursor. Utilization of carbon fibers in military aircraft has increased because of the advantage of lightweight strength and smooth outer construction. As carbon fiber applications expand, so does the probability of worker exposure via inhalation and skin contact.

Numerous in vitro and in vivo studies have been conducted to assess the health hazards from carbon fiber exposure. Modeling experiments based on equivalent aerodynamic diameters have demonstrated that diameter is the determinant of respirability

The limits of respirability for fibers is 3.5 μm diameter. The industry standard is 7-8 μm diameter which is outside the respirable range. Intratracheal and inhalation studies on carbon fibers and dust have not resulted in any deleterious changes; however, in one inhalation study the aerosol generated was particulate dust and not fibers In another subchronic inhalation study, rats were exposed to only one concentration of fibers preventing a dose-response evaluation. None of the studies adequately describe the particle size distribution.

Future inhalation studies need to characterize the fibers generated in terms of equivalent aerodynamic diameter. Mutagenicity tests with extracts of pitch-based carbon fibers elicited positive results in Sister Chromatid Exchange (SCE) and Unscheduled DNA Synthesis (UDS) tests and negative results in the Chinese Hamster Ovary (CHO) and Ames tests.

Extracts of PAN-based carbon fibers were negative in all these tests. Likewise, the pitch-based carbon fiber extracts produced positive results in a lifetime painting study in mice. Negative results were obtained with extracts from PAN-based carbon fibers in similar carcinogenicity testing in mice. Implant studies in rabbits, rodents and humans have resulted in little or no significant tissue reactions. In the hamster tracheal organ culture model, graphite fibers were compared to crocidolite asbestos and no significant cellular differentiation changes occurred after 1 and 3 weeks in culture; whereas, asbestos produced significant proliferative degenerative changes. Limited epidemiologic studies of carbon fiber production workers have shown no adverse pulmonary effects except for some skin irritation

Current industrial PAN-based carbon fibers do not appear to be a significant inhalation hazard nor are they biologically active in several in vitro test systems. Minor skin and eye irritancy can be prevented with physical protection (goggles and gloves) Since carbon fibers can absorb contaminant chemicals, future studies should assess each situation (eg , burn scenario) individually as to synergistic effects from chemical by-products, from the epoxy resins of the composite material, or from physical changes (reduction of diameter)

INTRODUCTION

It is appropriate that a conference on composite technology be hosted by Wright-Patterson Air Force Base since it is the birthplace of carbon fiber technology In the 1950s, the Air Force Materials Laboratory supported research on a Union Carbide process to develop rayon-based carbon fiber. This fiber was later replaced by higher yielding fibers from either petroleum pitch or polyacrlyonitrile (PAN). All of these fibers were synthesized by similar processes involving an oxidation stage to stabilize the fiber followed by carbonization and graphitization to eliminate noncarbon elements and to enhance mechanical properties (Donnet et al., 1984). The terms "carbon fiber" and "graphite fiber" are used synonymously, however, the distinction between the two is the temperature of pyrolization

The carbon fibers are heated to about 1500° C, while the graphite fibers are heat treated to about 2500° C resulting in a stronger crystalline fiber structure (Waritz, 1987) PAN-based fibers are the purer, more commonly used precursor. The lightweight, high tensile strength of these synthetic fibers makes them attractive for commercial applications such as sports equipment, reinforcing materials in structural composites, and prothestic devices for humans. Utilization of carbon fibers in military aircraft has increased because of

the advantage of lightweight strength and smooth outer-construction As these applications expand, so does the probability of worker exposure via inhalation and skin contact. This review will examine some of the toxicological data available to assess health hazards from carbon fibers.

Several excellent reports were used as sources of references (Dahlquist, 1984; Smith, 1986; Vu, 1988; Waritz, 1987). In addressing the larger issue of toxicology of composites, not only the carbon fiber and its precursor must be considered but also the surface activation, sizing, and the epoxy-type binders. The latter will be discussed by other speakers at this conference; this presentation is limited to carbon fibers.

AERODYNAMIC CONSIDERATIONS

One of the most important characteristics that must be described in any toxicological study involving a fiber has to be dimension. By definition, a particle is considered a fiber if its aspect ratio (length to diameter ratio) is greater than 3:1. It was the classical work of Stanton et al., (1972) that implicated fiber dimension as the culprit of carcinogenicity. Intraperitoneal injection of fibrous glass into rats produced mesothelioma similar to asbestos when the size of the fibrous glass was reduced to short, thin fibers. The Stanton hypothesis is based on dimension: fibers less than 0.25 μm diameter and greater than 8 μm length were considered carcinogenic.

Not only is fiber dimension critical in these in vitro studies, but it is also essential for credible inhalation studies. The aerodynamic equivalent diameter (Dae) is the determinant of respirability where Dae is defined as the diameter of a unit density sphere having the same terminal settling velocity as a given particle. If Dae is less than 10 μm, then it can be respirable, however, the majority of particles deposited in the alveoli are from 0.8 to 3 0 7 μm (Gross et al., 1984). A fiber which has an actual diameter of 3.5 μm has very little probability of reaching the alveoli regardless of how short it may be. As the length increases, the Dae increases and alveolar deposition decreases (Gross,1981). For example, if a fiber had an actual diameter of 3.5 μm, its Dae would be 7.8 μm if its length were 10 μm If the fiber length increased to 70 μm, that same fiber would then have a Dae of 10.4 μm; thus, a 3 5 μm fiber has very little probability of alveolar deposition. This theory is supported by studies on the size analysis of particles found in human lungs exposed to asbestos fibers; these studies indicate that the upper limits of respirable fibers are either 3.5 μm in diameter or 200

μm in length (Lee, 1985). Similar upper limits are seen with rodents exposed to asbestos, fiberglass, or mineral fibers. The retention of fibers less than 0.5 μm in diameter is significantly higher than for larger diameters with a peak of 7.6 percent with a fiber length of 21 μm. Fibers 1.0 μm in diameter with a fiber length of 5 μm had a maximum retention of 1 percent (Hammad et al.,1982). In deposition studies of glass fibers in rats, Morgan et al. (1980) concluded that fibers with diameters exceeding 2 μm and with aspect ratios greater than 10 would be virtually nonrespirable to rats and that it is generally assumed that the corresponding value for man is 3 μm diameter.

INHALATION STUDIES

Few inhalation studies specifically conducted on carbon fibers can be found in the literature. Holt and Horne (1978, 1982) conducted several inhalation studies on dust from carbon fiber. Guinea pigs were exposed for 7 to 104 hours to PAN-based chopped fibers described as RAE type 2. The chopped fibers had been further reduced by a hammer mill, resulting in an aerosol of 98.8 percent nonfibrous particles (1 μm diameter) and 1.2 percent fibers of varying dimensions: 10 μm diameter with lengths greater than 100 μm; fibers 1 to 2.5 μm diameter with lengths up to 15 μm; and transparent fibers 1.5 μm diameter with lengths up to 30 μm.

Their results showed that macrophages readily phagocytized the dust particles even up to 100 days following exposure. The few fibers seen were still extracellular after 27 weeks, and no pathological effects were seen from carbon fiber dust in any of their experiments. This slow, continual dust clearance is similar to the studies on graphite dust reported by our laboratory (Thomson et al., 1987 and 1988). We also found a continual macrophage clearance of graphite dust three months following acute and repeated exposures with no apparent adverse pathology.

Only one inhalation study has been published (Owen et al., 1986) in which carbon fibers were actually generated and comprised the test aerosol. This was a single concentration (20 mg/m^3) subchronic study. Rats were exposed to pulverized Celion, PAN-based carbon fiber for 6 hour/day, 5 days/week for 16 weeks. Rats were killed at 4, 8. 12 and 16 weeks of exposure and after a 32-week postexposure recovery. Exposed rats were compared to air-exposed controls for pulmonary function and histopathological change. There were no consistent, significant pulmonary function changes and no evidence

of fibrosis or inflammation. Alveolar macrophages were seen containing fiber particles. The aspect ratio of the generated particles was reported to be 20 to 60 μm long with 7 μm diameters. Fiber length was determined by gently tapping one filter onto a glass slide and counting the number of fibers in various size ranges.

Although this study did not show any deleterious effects from inhalation of carbon fibers, there are several unanswered questions in the experimental design. The sampling techniques did not measure the aerodynamic equivalent diameter; in fact, the method described probably missed any smaller diameter or shorter length fibers that may have been present in the pulverized aerosol. The gravimetric concentration did not represent a respirable concentration which was probably lower than the measured 20 mg/m^3. All of the published modeling experiments by Timbrell (1982), Harris (1976) and studies by Morgan (1980) and Hammad (1982) question the respirability of a 7 μm diameter fiber. Although this was a single dose study and no dose-response effects could be evaluated, it did demonstrate that inhalation of low concentrations of PAN-based carbon fibers did not result in any adverse pathological changes in rats. Another single dose industry sponsored inhalation study on 3.5 μm diameter carbon fiber has been conducted but has not been published yet (personal communication, Waritz, 1988). After this study is published and evaluated, additional multiple dose inhalation studies should be conducted to fill any data gaps. Future inhalation studies should address sampling techniques to measure aerodynamic equivalent diameter such as that described by Liu et al. (1983). Another consideration should be the choice of species. Vu (1988) noted that rodents are obligatory nose breathers and have a greater filtering capacity than humans.

Inhalation tests in rodents may underestimate the hazard potential of fibers to humans unless the deposition of fibers is comparable to positive controls.

INTRATRACHEAL/INTRAPERITONEAL STUDIES

Characterization of carbon fibers during generation, machining, or incineration is an essential prerequisite for any toxicological study. A major concern is under what conditions fibrillation (longitudinal fracture) can occur. Any reduction in diameter would result in making the carbon fiber more respirable. A number of tests were conducted by the U.S. National Aeronautics and Space Administration (NASA) in 1979-1980 to ascertain the extent of carbon fiber release during an aircraft crash. Dahlquist (1984) has reviewed this issue, and other

speakers will discuss it at this conference. It appears that reduction of diameter does occur with incineration. The hazards from those reduced incinerated particles were evaluated in a series of intratracheal/intraperitoneal studies conducted by the US Air Force Aerospace Medical Research Laboratory (Parnell, 1985).

Samples of Hercules AS-1 and AS-4 carbon fibers, which are used in the composite materials for the F-16, were cut into lengths of 5 centimeters and oxidized in a furnace at 575° C for 4 hours. These samples were examined by scanning electron microscopy (SEM), and the fibers were counted and grouped according to diameters into the following categories: 1 μm, 1-2 μm, 2-5 μm, and greater than 5 μm. Fiber lengths were not measured. Male Fischer 344 rats were injected with suspensions of these reduced fibers via two routes: intratracheal and intraperitoneal. The intratracheal treated rats were evaluated at 100, 200 days, 1 and 2 years following exposure. Bronchial ulcerations were reported at 100 days and 2 years, but these lesions were also present in the controls. There were no treatment related pulmonary tumors. The intraperitoneal treated rats were evaluated at 200 days and 2 years following exposure. Degenerative and neoplastic changes were reported in both control and exposed rats at two years; these lesions are common in aged rats. There were no mesotheliomas. The significance of this study was limited by the small numbers of rats in the experimental groups.

Fibrillation of carbon fibers from machining does not seem to occur Lurker et al. (1985) reported no reduction in diameter of 14 industrial hygiene samples from machining of composites at Wright-Patterson AFB. Boatman et al. (1988) collected dust from several different kinds of machining operations of composite fiber-epoxy materials. Respirable fractions from the bulk dust were generated and their aerodynamic, chemical, and morphological characteristics evaluated. Few fibers were produced, and none had reduced diameters. Rats were exposed to a single intratracheal dose (5mg), and the histopathological (Luchtel et al.,1988) and cytotoxicological responses (Martin et al., 1988) were evaluated. Six composite dust were compared to a saline/solvent control, a negative control (aluminum oxide), and a positive control (quartz). Of the six dust tested, four produced small fibrotic nodules in the lung less severe than the quartz. Martin's studies compared these same composite materials and controls in vitro using rabbit alveolar macrophages and in vivo using direct intratracheal injection into rat lungs. Macrophage viability, cytotoxicity and cellular changes in the lavage fluid were used as indices of

damage. Three of the composite samples showed little toxicity, but two were significantly more toxic than controls. Martins's results were not in complete agreement with those of Luchtel; however, these studies do emphasize the fact that the epoxy and curing agent chemical composition can influence the toxicity of the neat PAN-based carbon fiber. It appears this is the first animal study to evaluate the pulmonary effects of exposure to composite dust rather than just carbon fiber. The problem with intratracheal and intraperitoneal studies is that the route of exposure is non-physiological. Oftentimes non-respirable particles are forced down the lungs in an artifactual distribution pattern; however, in this series of studies, only respirable fractions were used. As a preliminary "worse case" scenario, these results indicate that further inhalation studies should be conducted to clarify the risks of respirability of these composite fibers.

IN VITRO STUDIES

Conflicting results have been reported by Vu (1988) in regard to cytotoxicity studies on carbon fibers. In some studies the fibers were non-hemolytic to rabbit erythrocytes but cytotoxic in the rabbit alveolar macrophage (RAM) test. The discrepancy may be related to differences in fiber type and/or size distribution of the test materials. In many studies there are insufficient experimental details to characterize the type, treatment, and size of carbon fibers tested. Koschier et al. (1984) reported that graphite fibers had no detectable cytotoxicity in the RAM test when compared to crystalline silica using cell viability and ATP content as criteria of cytotoxicity. They used PAN-based graphite fibers with a reported dimension of 0.1 to 1.5 mm which I assume was the length and not the measured diameters.

Mossman (1977) and Woodworth (1983) have demonstrated the efficacy of using the hamster tracheal organ culture model as a short-term in vitro assay to predict pathological and cytotoxic potential of fibrous and particulate xenobiotics. Our laboratory had Battelle Columbus assess this model as an alternative toxicological testing method to predict the potential health hazard of particulate materials (Placke et al.,1987). PAN-based graphite fibers were compared to crocidolite asbestos and several other fibrous and particulate materials. The fibrous materials were ground with mortar and pestle to produce a material acceptable to cell culture. The graphite fibers had a mass median diameter of 10 4 μm (geometric standard deviation of 1.5) and an aspect ratio of 3.3. After one and three weeks

in culture, there were significant proliferative, degenerative changes with asbestos while there were no significant cellular differentiation changes with the graphite fibers.

Waritz (1987) has described unpublished mutagenicity studies conducted by Hercules Inc. on their PAN-based carbon fibers which were ground and unsized. Benzene extracts were incubated with the five Ames tester strains of S. typhimurium, and there were no increases in reversions. Analysis of the extracts for polynuclear aromatic hydrocarbons (PNAs) found no PNAs by a method sensitive to 50 ppb. Our laboratory has conducted similar Ames assays on PAN-based Celion carbon fibers, only we extracted with dichloroethane and resuspended in DMSO with negative results.

Union Carbide reported to EPA the results of mutagenicity and genotoxicity studies on PAN- and Pitch-based carbon fibers. Smith (1986) has reviewed these studies in detail. The fibers were ground, extracted with benzene, then resuspended in acetone for testing in the sister chromatid exchange assay (SCE), unscheduled DNA synthesis assay (UDS), Chinese hamster ovary assay (CHO), and the Ames test. Results for the pitch-based fibers were: positive in the SCE with and without metabolic activation producing numerous chromosomal aberrations; positive in UDS; no effect in CHO with and without metabolic activation; and negative in the Ames test with and without metabolic activation. Similar tests on PAN-based extracts produced negative results in all the above assays. It appears the benzene extracts from pitch-based carbon fibers contained clastogenic and mutagenic material.

CARCINOGENICITY STUDIES

Union Carbide conducted a two-year life-time skin painting study in mice to assess the potential of four types of carbon fibers in inducing cancer. These studies were reviewed in detail by Smith (1986) and Vu (1988). The four fibers tested were: 1) petroleum pitch-based continuous fibers (CF), 2) petroleum pitch-based short fibers (MAT), 3) PAN-based oxidized, 4) PAN-based continuous fibers. Groups of 40 mice were painted three times per week with a 10 percent benzene solution of each of the ground fibers for over two years. None of the 285 historical benzene controls had tumors. In the methylcholanthrene positive controls, 37/40 developed squamous cell carcinomas. In the CF pitch-based group, 1/40 developed papillomas, and 1/40 had squamous cell carcinoma at the site of application. The incidence of tumors in the CF group was considered biologically but not statistically significant. A low incidence of remote atypical tumors were found in 3/40 of the

pitch-based MAT fibers and 2/40 in the PAN oxidized. There were no tumors in the PAN-based carbon fiber group. The pitch-based carbon fibers were considered to be oncogenic under the conditions of the test.

Other chronic implant studies have been conducted to evaluate the oncogenic potential of carbon fibers. Neugebauer et al. (1981) injected carbon fragments into the bone marrow of rabbits and after two to twelve weeks examined the femur and parenchymal organs (lung, liver, spleen, kidneys) for histopathological changes. There was new formation of bone with inclusion of fiber fragments. No inflammation, necrosis, or foreign body reaction was detected. Fiber fragments were detected in the lungs, liver, and spleen without adverse reaction.

Tayton et al. (1982) conducted several experiments in rats to investigate the carcinogenic potential of carbon fiber in strand or powdered form. Intramuscular implantation or injection was conducted with comparison implants of blackbraided silk suture as controls After 18 months, the rats were killed and evaluated histopathologically. There was no evidence of malignant changes and only minimal tissue reaction less severe than the black silk controls.

EPIDEMIOLOGY

Jones et al. (1982) have an ongoing survey of workers in a carbon fiber production plant. Spirometric and chest radiographic evaluations were obtained from 88 employees. There were no pulmonary function abnormalities, and no evidence of dust-related disease was seen in x-rays. Dust samples collected showed that respirable particles were nonfibrous and composed of resin sizing and extraneous materials. Fibers collected had diameters of 8-10 μm with no evidence of fibrillation.

Dahlquist (1984) described the results of a Russian survey that reported dermal problems experienced by newly hired personnel in carbon manufacturing plants.

OTHER STUDIES

In view of the possibility of skin/eye irritation, our laboratory conducted rabbit eye/skin irritation tests on PAN-based Stackpole carbon fibers (Panex, 8 μm diameter) The fibers were ground with mortar and pestle, and 500 mg was placed on clipped rabbit skin with 2 ml sterile water. After four hours, the fibers were removed with water, and no skin irritation was

observed. For the eye irritancy test, the ground fibers (0.1 ml) were placed into one eye sac of six rabbits. After one hour, 5/6 had conjunctival redness, 6/6 mild to moderate chemosis, and 5/6 had tearing. After 24 hours, the fibers were rinsed out, and 3/6 eyes were mildly opaque, all six had mild to moderate redness and chemosis. The carbon fibers were graded as a moderate eye irritant; all effects were reversible by seven days.

American Cyanamid, PAN-based, graphite fibers were also tested in our laboratory for acute aquatic toxicity using the cladoceran, Daphnia magna, and the algal species, Ankistrodesmus falcatus. The fibers were ground to a fine powder with mortar and pestle and sonicated to maintain them in suspension for testing. The graphite fiber particles did not inhibit growth of the algal species nor was it toxic to Daphnia magna. This material would be assigned a score of 1-3 according to a draft scoring criteria for aquatic toxicity published by USEPA. In comparison, a positive control (brass dust) was also tested and would be assigned a score of 9 for both daphnids and algae.

CONCLUSIONS

Available data reviewed indicate that no adverse health effects occur from exposure to PAN-based carbon fibers. Carbon fiber is not classifiable as a human carcinogen since there is inadequate evidence of carcinogenicity from animal studies and no human data. However, pitch-based carbon fibers may be suspect since positive clastogenic effects were produced in genotoxicity tests, and positive results were reported from a dermal, lifetime painting study ir mice.

In assessing the health hazard potential of carbon fibers, the precursor, heating history, epoxy matrix, sizing, aerodynamic equivalent diameter, and length all need to be characterized. Currently, there is no evidence that the industry standard PAN-based carbon fiber with diameters 7-8 μm are a respiratory hazard. An additional industry sponsored subchronic inhalation study on a 3.5 μm diameter, PAN-based carbon fiber has been conducted but is not available for publication yet. Once this study has been evaluated, additional work may be required.

REFERENCES

Boatman, E.S., Covert, D., Kalman, D., Luchtel, D., (1988). Physical, morphological, and chemical studies of dust derived from machining of composite-epoxy materials. Environ. Res. 45:242-255.

Dahlquist, B.H., (1984). Evaluation of Health Aspects of Carbon Fibers, Master of Science Thesis, Dept. Environ. Sci. & Eng., School of Public Health, Univ. N.C., Chapel Hill, N.C.

Donnet, J.B., Bansal, R.C., Carbon Fibers. Marcel Dekker Inc., N.Y., 1984.

Gross, P., (1981). Consideration of the Aerodynamic Equivalent Diameter of Respirable Mineral Fibers. Am. Ind. Hyg. Assoc. J., 42:449-452.

Gross, P., Braun, D.C., (1984). Toxic and Biomedical Effects of Fibers, Noyes Publ., Park Ridge, N.J.

Hammad, Y., Diem,J., Craighead, J., Weill, H., (1982). Deposition of Inhaled Man-Made Mineral Fibres in the Lungs of Rats. Ann. Occup. Hyg., 26:179-187.

Holt, P.F., Horne, M., (1978). Dust from Carbon Fibre. Environ. Res., 17:276-283.

Holt, P.F., (1982). Submicron Carbon Dust in the Guinea Pig Lung. Environ. Res., 28:434-442.

Johnson, D.W., Landis, W.G., (1988). The acute, aquatic toxicity of selected mineral particles. CRDEC-TR-88143, APG,MD.

Jones, H.D., Jones, T.R., Lyle, W.H. (1982). Carbon Fibre: results of a survey of process workers and their environment in a factory producing continuous filament. Ann. Occup. Hyg. 26:861-868.

Koschier, F.J., Friedman, M.A., Davis, R.A., Gay, R., (1984). Rabbit alveolar macrophage (RAM) cytotoxicity assay performed on metal coated graphite fibers. Toxicologist, 4:2.

Lee, K.P., (1985). Lung Response to Particulates with Emphasis on Asbestos and Other Fibrous Dusts. CRC Crit Rev Toxicol, 14(1):33-86.

Luchtel, D.L., Martin, T.R., Boatman, E.S. (1988). Response of the rat lung to respirable fractions of composite fiber-epoxy dusts. Environ.Res.: accepted for publ. 1988.

Lurker, P.A., Olson, C.T., Weigl, R.W., (1985). Industrial hygiene aspects of carbon composite aircraft components. Presented at American Industrial Hygiene Conference

Martin, T.R., Meyer, S.W., Luchtel, D.R., (1989). An Evaluation of the Toxicity of Carbon Fiber Composites for Lung Cells in vitro and in vivo, accepted for publication Environ. Res.

Morgan, A., Black, A., Evans, N., Holmes, A., Pritchard, J.N., (1980) Deposition of Sized Glass Fibers in the Respiratory Tract of the Rat. Ann. Occup. Hyg., 23:353-366.

Mossman, B.T., Kessler, J.B., Ley, B.W., Craighead, J.E.,(1977) Interaction of crocidolite asbestos with hamster respiratory mucosa in organ culture. Lab. Invest. 36:131-139.

Neugebauer, R., Helbing, G., Wolter, D., Mohr, W., Gisinger, G., (1981). The body reaction to carbon fibre particles implanted into the medullary space of rabbits. Biomaterials 2:182-184.

Owen, P.E., Glaister, J.R., Ballantyne, B., Clary, J.J.,(1986). Subchronic Inhalation Toxicology of Carbon Fibers. J. Occup. Med., 28:373-376.

Parnell, M., (July 1987). Current application and studies on health effects of carbon fibers - military point of view. Presented at the Toxicology Forum, Aspen, CO.

Placke, M.E., Fischer, G.L., (1987). in vitro toxicity evaluation of ten particulate materials in tracheal organ culture. CRDEC-CR-88010, APG, MD

Smith, L.H., (1986). Carbon Fibers Health Effects, Preliminary Draft prepared by Oak Ridge National Laboratory for EPA.

Stanton, M.F., Wrench,C., (1972). Mechanisms of Mesothelioma Induction With Asbestos and Fibrous Glass. J Nat Cancer Inst 48:797-821

Thomson, S.A., Burnett, D.C., Anderson, R.S., Hilaski, R.J., (1987). Pulmonary and Pathological Responses of Synthetic Graphite. Toxicologist, 7:199.

Thomson, S A , Crouse, C L., Burnett, D.C , Hilaski, R.J., (1988) Repeated Inhalation Toxicity Study of Synthetic Graphite in Rats. Toxicologist, 8:1004

Timbrell, V., (1982). Deposition and Retention of Fibers in the Human Lung. Ann Occup. Hyg., 26:347-369.

Timbrell, V. (1965). The Inhalation of Fibrous Dusts. Ann N Y. Acad Sci., 132:255-273.

Vu, V.T., (1988). Health Hazard Assessment of Nonasbestos Fibers Final Draft, Office of Toxic Substances, US EPA, Wash. D C.

Waritz, R.S., (July 1987). Carbon Fibers-General Toxicology, presented at Toxicology Forum, Aspen, CO.

Woodworth, C.D., Mossman, B.T., Craighead, J.E. (1983). Induction of squamous metaplasia in organ cultures of hamster trachea by naturally occurring and synthetic fibers. Cancer Res. 43:4906-4812.

SAFE USE OF KEVLAR® ARAMID FIBER IN COMPOSITES

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ABSTRACT

Although Kevlar® aramid fiber can be broken into respirable size subfibers (fibrils), the fibrils' low airborne concentrations and low toxicity permit Kevlar® to be used in composite manufacturing operations without undue health risk to aerospace workers. Inherent fiber properties yield consistently low airborne fibrous dust levels. Measured exposure levels from industrial operations have not exceeded 0.3 fibrils/ml, 8-hour, time-weighted-average (TWA), and composite machining is typically 0.2 fibrils/ml or less.

Animal and human skin tests show no potential for sensitization, and low potential for irritation. Rat testing with nonfibrous polymer particles of Kevlar® show no permanent toxic effects from high dose feeding, inhalation, or intratracheal instillation.

Using special techniques to generate high levels of respirable fibrils for rat inhalation testing, two-week exposures at extreme doses produced slight lung scarring, which shrank with recovery. No permanent lung damage occurred below approximately 1400 times typical workplace levels. Two-year doses (500 times workplace levels) produced lung tumors of a type not seen in man, and slight lung scarring. Below about 100 times typical work levels no permanent lung damage was seen. Based on long-term rat inhalation results, Du Pont recommends an acceptable exposure limit for Kevlar® of 5 f/ml, 8-hour TWA. Normally, good industrial ventilation of composite machining operations should maintain shops well below that level

INTRODUCTION

Kevlar® aramid is a lightweight organic fiber used extensively in aerospace composites because of its high specific stiffness, strength, and toughness. The highly oriented, crystalline substructure responsible for its high properties, also makes it possible to peel subfibers (fibrils) from the base fiber by surface abrasion, cutting, or fracturing. Because these subfibers can be of respirable size (3 micrometers diameter and 60 micrometers long) Du Pont has conducted tests to determine that they do not pose a significant hazard to

human health. Since hazard is a function of exposure and toxicity, both have been studied by Du Pont's Haskell Laboratory for Toxicology and Industrial Medicine.

The following summary of these studies shows that industrial operations with Kevlar® produce only low levels of airborne respirable fibrils, and animal studies indicate minimal potential toxicity for man. Nevertheless, exposure to durable, respirable dust of any kind should be minimized, and an acceptable exposure limit (AEL) for Kevlar® has been set on the basis of the long-term animal inhalation tests. It will be shown that normal, good industrial hygiene permits Kevlar® to be controlled to levels well below the AEL. Consequently, it can be readily used in composite manufacturing operations, as it has been for over 16 years without undue health risk to workers.

FIBER STRUCTURE

Kevlar® aramid fibers are spun as continuous yarns with individual filaments that are too large in diameter to be respirable - nominally 12-15 micrometers. But their unique substructure has long, highly oriented crystal domains that are strong longitudinally, but relatively weakly bonded together. These subfibers, called fibrils, are about 0.1 micrometer in diameter. Shear can break down the filament into single or bundled fibrils that can be of respirable size. Most are highly complex, ribbon-like in shape, and branched and curled. The surface has high static charge, especially in dry atmospheres. The mechanical entanglement and electrostatic attraction predisposes fibrils to clump together into nonrespirable clusters. As a result of these inherent characteristics, there are more nonfibrous particles than fibrils in the airborne respirable dust produced by abrading the fiber, or machining a composite containing them.

AIRBORNE FIBRIL EXPOSURE MEASUREMENTS

Levels of airborne Kevlar® fibrils have been measured in Du Pont's own manufacturing processes for fiber and pulp, and in the mills of customers using them. The measurements are made using NIOSH 7400 (NIOSH, 1984), in which fibrils are captured on filter paper by a calibrated air pump, then counted by polarized light microscopy. (This is the standard method for measuring asbestos fibril levels.) Only respirable fibrils are counted, and reported as fibrils per ml of air.

Numerous industrial processes have been monitored, including cutting, staple yarn spinning, filament yarn twisting, roving, winding, and weaving, friction material mixing and grinding, and gasket sheet making and cutting. The maximum personal exposure to date has been 0.28 f/ml, 8-hour, time-weighted average (TWA). Composite machining, and clutch facing grinding, processes where Kevlar® fiber is a major portion of the material being cut, have levels below 0.2 f/ml, while continuous filament handling generates less than 0.1 f/ml, the limit of reliable measurement. In area measurements made near dust-producing equipment, it has been found that momentary levels of airborne fibrils can be increased up to ten times when an air hose has been used for clean-up. Although eight-hour TWA fibril levels remained low, airjet use should obviously be avoided to minimize suspending respirable dust Waterjet cutting fluid used to cut Kevlar® contains respirable fibrils that may become airborne in an aerosol; monitoring is planned.

TOXICOLOGICAL TESTING

Since 1972, when Kevlar® was first commercially used in volume, Haskell Laboratory has studied the toxicological properties of Kevlar® as polymer particles, as whole fibers and as fibrils. Polymer particles were tested to determine what chemical toxicity Kevlar® might have, as distinct from the shape-dependent effects of fibers.

Fiber Dermal Exposure Tests

Skin contact tests with animals and several hundred human volunteers have shown no potential for sensitization (chronic allergic reaction) and low potential for skin irritation (Reinhardt, 1980). In the few cases where workers had mild skin irritation, it resulted from simple mechanical abrasion from fiber accumulations under tight clothing Improved personal hygiene and loose fitting, clean work clothes relieved the irritation.

Polymer Feeding Tests

Kevlar® polymer has low oral toxicity (Reinhardt, 1980) In tests where rats were fed nonfibrous polymer particles the maximum tolerated dose was found to be above 7500 mg/kg, the limit of the test.

Polymer Inhalation and Instillation Tests

The polymer does not have significant toxic effect on lung tissue (Reinhardt, 1980) In inhalation tests rats were exposed to doses of 130 mg/cu m of polymer for two weeks with two weeks recovery. In a longer term test, 25 mg of polymer particles were instilled into the lungs of rats that were allowed to recover up to 21 months In both tests, nonspecific lung reactions were the only response observed

Fibril Inhalation Testing

Because of the low level of airborne respirable fibrils generated by commercial products of Kevlar®, special techniques were developed to reach extreme concentrations for inhalation testing. A superfine test material of essentially all fibrils was made, and a high pressure air mill was used to suspend and extract respirable fibrils Airborne fibril levels up to an estimated 200 f/ml were generated for short-term (2-week exposure) tests, and up to 400 f/ml for long-term (12- to 24-month exposure) tests. In all inhalation tests rats were exposed 6 hours/day, 5 days/week and examined for clinical and histopathological effects

In short-term tests (Lee et al., 1983), rats were exposed for two weeks then sacrificed periodically for up to six months. At the highest exposure, an estimated 1000-2000 f/ml, or about 10,000 times the maximum fibril levels measured in composite machining, slight lung scarring (fibrosis) was seen The scarring shrank during recovery, indicating the fibrosis is nonprogressive (i.e., unlike silicosis, where scar tissue continues to grow after exposure ceases.) At 280 f/ml (about 1400 times the maximum workplace concentration for composites) and below, no permanent lung damage was seen, with the behavior approximating that of a nuisance dust

In long-term tests (Lee et al., 1988), rats were exposed for one year at the maximum dose of 400 f/ml, with up to one-year recovery. The exposure was stopped at one year because the dose was high enough to cause many animals to die from suffocation caused by closure of the finest lung passageways When the exposure stopped, the rats' mortality rate returned to normal At 100 f/ml, 25 f/ml and 2.5 f/ml exposures were for the full two years, the normal rat lifespan.

At 100 f/ml and 400 f/ml, 11 rats of 229 developed lung tumors The tumors were of a type not found in man (cystic keratinized squamous cell carcinoma) These tumors have been seen in similar, high-dose exposures of rats to other, benign dust; they do not

metastasize, and were not the cause of rat deaths. Haskell concludes that the relevance of this type of tumor to human health risk is minimal.

Of particular significance was the finding that long fibers (generally considered to be more damaging than short fibers for any material) are either broken down or cleared from the lungs preferentially. The average fiber length in the lungs fell from 12 to 5 micrometers during the test. Also, fibers were not found to have migrated from the lungs to other sites in the body. The mechanisms of lung clearance of Kevlar® is the subject of a test just beginning at Haskell Lab.

At 25 f/ml and above, lung scarring proportional to exposure concentration was observed; because the degree of scarring is only slightly above that of controls at 25 f/ml, doses below that are considered to be "no effect" levels. Rats dosed at 2.5 f/ml, had no lung scarring.

INDUSTRIAL HYGIENE RECOMMENDATIONS

Monitoring and Control

On the basis of the long-term tests above, Haskell set (in 1985) an acceptable exposure limit (AEL) at 5 f/ml, 8-hour TWA; Du Pont recommends this control limit to those who use Kevlar® (letter, Reinhardt, 1985; MSDS, I. E. Du Pont) Operations with dusting potential should be monitored using method NIOSH 7400. By local exhausts at equipment for machining composites containing Kevlar®, and by good ventilation of the work area, airborne fibril levels can be readily maintained at less than 0.5 f/ml - well below the AEL

Preventing Skin Abrasion

While few people have complained of skin irritation, workers can avoid mechanical skin abrasion by fibers and dust by wearing loose fitting work clothes and washing themselves and their clothes regularly.

Clean-up and Disposal

Keep dust from building up by regular vacuuming with a vacuum cleaner having a high efficiency filter to remove the collected fibrils. Do not use an air jet to blow off machines. Waste fibers and dust of Kevlar® may be disposed of as ordinary waste

SUMMARY

Kevlar® aramid fibers can be used in composite operations without undue health risk to workers. The fibers do not have potential for skin sensitization, and are unlikely to produce skin irritation from purely mechanical abrasion. While Kevlar® fibers are too large to be inhaled, they may be fractured into respirable fibrils in some of the manufacturing processes used with composites. Industrial process monitoring shows that airborne respirable fibril levels are low in typical operations. While animal testing shows that permanent lung damage can occur from fibril inhalation, it is only at continuous exposures many times the maximum airborne concentrations measured in the workplace. Du Pont recommends an AEL of 5 f/ml, 8-hour TWA - a level well above that readily achieved by normal, good exhaust and ventilation of composite machining operations.

REFERENCES

Lee, K.P , Kelly, D P., and Kennedy, G.L., Jr. (1983). Pulmonary Response to Inhaled Kevlar® Aramid Fibers in Rats. Tox. and App. Pharm., 71, 242-253.

Lee, K.P , Kelly, D.P., O'Neal, F.O., Stadler, J.C., and Kennedy, G.L., Jr. (1988). Lung Response to Ultrafine Kevlar® Aramid Synthetic Fibrils Following 2-Year Inhalation Exposure in Rats. Fund. & Appl. Tox., 11, 1-20.

Letter, April 4, 1985, C.F. Reinhardt to Document Control Officer (WH-557), O.T.S./U.S.E.P.A., reporting findings of long-term testing.

Material Safety Data Sheet, Kevlar® Aramid Fiber, (1985). E. I. Du Pont de Nemours & Co., Wilmington, DE.

Nat'l. Inst. Occ Safety & Health (1984); NIOSH Manual of Anal Methods, 3rd Ed. (DHHS/NIOSH pub. 84-100.) Washington, D.C., Gov't Printing Office.

Reinhardt, C.F., Toxicology of Aramid Fibers (1980). In Proceedings of the National Workshop on Substitutes for asbestos, pp. 443-447, U S Environmental Protection Agency, Washington, D C.

FIBERGLASS CONTAINING COMPOSITE MATERIAL

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ABSTRACT

Fiberglass is one member of a family of products known collectively as man-made vitreous fibers because of their synthetic amorphous, glassy nature. Glass fibers will not burn, rot, or absorb moisture or odors. Fiberglass is generally supplied in two basic forms. wool-type fibers and textile (continuous filament) fibers.

Textile glass fibers, the type used in composite reinforcement, differ from the wool type in that they are die-drawn rather than spun. This manufacturing process results in a very uniform diameter for textile glass fiber products. Practically all fiberglass for composite reinforcement is greater than six microns in diameter. This diameter size fiber does not reach the deep lung areas (non-respirable fiber). Glass fibers break only into shorter fragments with the same diameter. Their diameters cannot be reduced by machining, milling or other mechanical processes.

Textile fibers destined for reinforcement applications are coated with a polyvinyl acetate-chrome chloride, polyvinyl acetate-silane, polyester-silane, or epoxy-silane size appropriate to the reinforcement application.

Exposure to glass fibers may cause mechanical irritation of the eyes, nose, and throat. A potential for skin sensitization can occur from the uncured resins and hardeners used in manufacturing the laminate. At times, this can be confused with the mechanical irritation caused by the fiberglass. Potentially dry but not cured epoxy-compatible sizing on the textile glass fiber could cause a skin sensitization reaction in the laminate fabricator Such a reaction is rare even though it has been reported to occur

In June 1987, the International Agency for Research on Cancer (IARC) categorized fiberglass continuous filament as not classifiable with respect to human carcinogenicity (Group 3) The evidence from human as well as animal studies was evaluated by IARC as insufficient to classify fiberglass continuous filament as a possible, probable, or confirmed cancer causing material. Fiberglass wool (primarily used for insulation in a variety of applications) was classified as a possible human carcinogen by IARC. (Group 2B) This

classification was substantially based on experimental animal studies in which they were exposed to wool glass fibers through non-natural routes, such as injection or implantation.

FIBERGLASS CONTAINING COMPOSITE MATERIAL

INTRODUCTION

Fiberglass is one member of a family of products known collectively as man-made mineral fibers because of their synthetic amorphous, glassy nature. Glass fibers will not burn, rot, or absorb moisture or odors. Fiberglass is generally supplied in two basic forms. wool-type fibers and textile (continuous filament) fibers.

The main health issue surrounding fiberglass is will its fibrous character cause the material to induce lung cancer in man. In order for a material to cause cancer it must reach the target tissue, in this case the deep lung tissue. The ability of any fiber to reach the deep lung tissue (respirability) is directly related to the diameter of the fiber. Fibers greater than about three microns in diameter do not reach the deep lung tissue (nonrespirable). Textile fiberglass used for composite reinforcement has a diameter which is too large to be respirable

MANUFACTURING PROCESS

Textile glass fibers, the type used in composite reinforcement, differ from wool fibers in that they are die-drawn rather than spun. This manufacturing process results in a very uniform diameter for textile glass fiber products. Practically all fiberglass for composite reinforcement is greater than six microns in diameter (see Fig. 1). Airborne fiber of this diameter does not reach the deep lung areas (non-respirable fiber). Glass fibers break only into shorter fragments with the same diameter (2). Their diameters cannot be reduced by machining, milling or other mechanical processes. This finding also holds true for fibers embedded in the laminate (1), (3)

Textile fibers destined for reinforcement applications are coated with a polyvinyl acetate-chrome chloride, polyvinyl acetate-silane, polyester-silane, or epoxy-silane size appropriate to the reinforcement application (9).

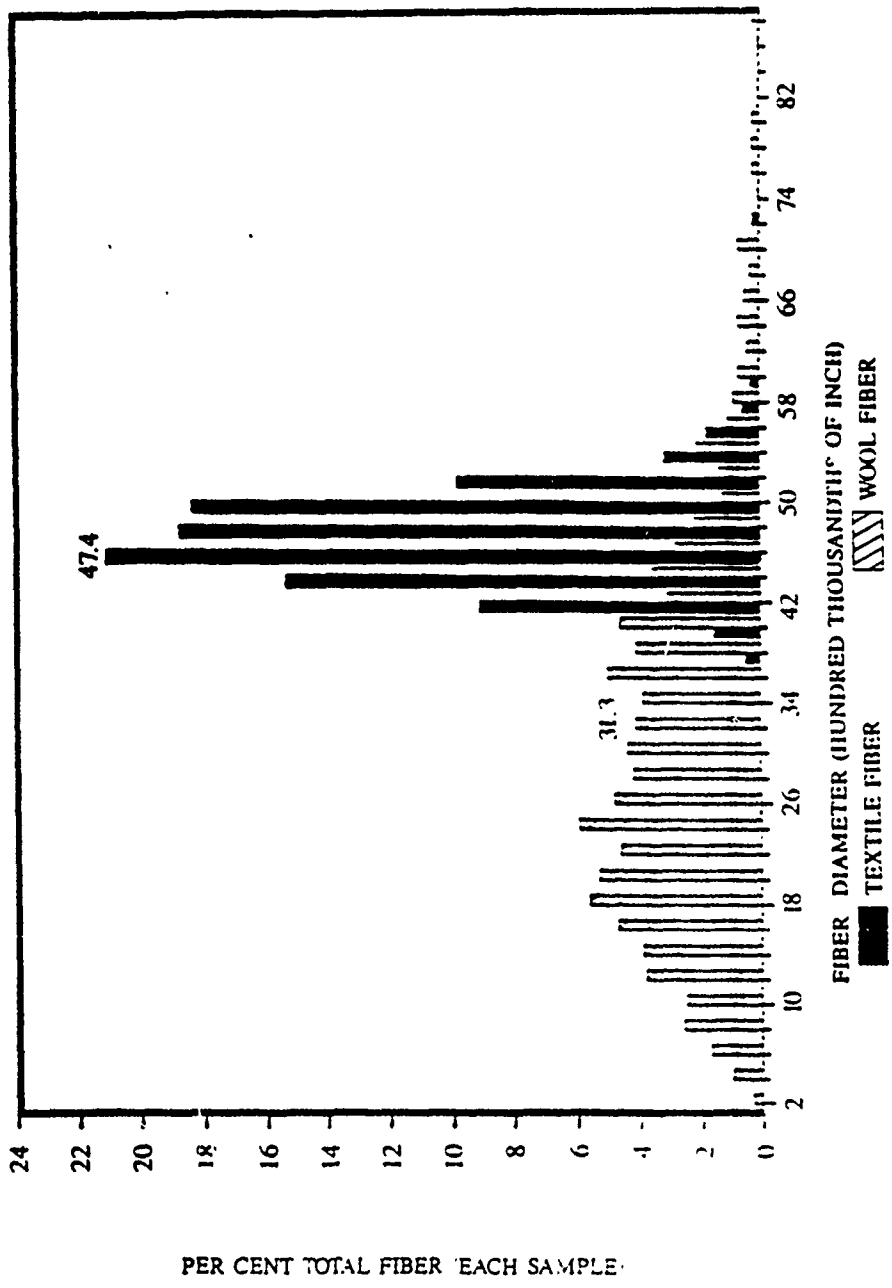

Figure 1 Wool and textile typical fiber diameter distribution

AIRBORNE EXPOSURES

The airborne exposures in the textile manufacturing plants were evaluated in conjunction with the epidemiological studies both in the United States and in Europe. The airborne exposures for fibers less than 3 microns in diameter (respirable fibers) in the different work areas in the plants ranged in mean exposure levels from 0.001 to 0.022 fiber per cubic centimeter (f/cc) in the European plants(10) and from 0.001 to 0.050 f/cc in the U.S. plants.(6) Most areas demonstrated airborne levels of less than 0.01 f/cc (see Table 1).

It is important to remember that these reported concentrations were for all fibrous particles and did not report only respirable textile glass fibers.

At these very low airborne fiber concentrations, non-glass fibers could make up an appreciable fraction of the airborne fiber concentration. A recent study carried out by Owens-Corning in our textile fiberglass manufacturing plants did not measure any airborne respirable textile glass fibers (see Table 2) (8). Similarly, airborne fiber sampling in operations where laminates are being cut, drilled, or sanded do not demonstrate respirable textile glass fibers (1).

EFFECTS OF EXPOSURE

Exposure to glass fibers may cause mechanical irritation of the skin, eyes, nose, and throat (7). A potential for skin sensitization can occur from the uncured resins and hardeners used in manufacturing the laminate. At times, this can be confused with the mechanical irritation caused by the fiberglass. Potentially, dry but not cured epoxy-compatible sizing on the textile glass fiber could cause a skin sensitization reaction in the laminate fabricator. Such a reaction is rare even though it has been reported to occur (4)

In June 1987, the International Agency for Research on Cancer (IARC) categorized fiberglass continuous filament as not classifiable with respect to human carcinogenicity (15) The evidence from human as well as animal studies was evaluated by IARC as insufficient to classify fiberglass continuous filament as a possible, probable, or confirmed cancer causing material.

Fiberglass wool (primarily used for insulation in a variety of applications) was classified as a possible human carcinogen by IARC (15). This classification was based substantially on experimental animal studies in which they were exposed to wool glass fibers through non-natural routes, such as injection or implantation.

TABLE 1. AIRBORNE FIBER LEVELS
(fibers per cubic centimeter)

UNITED STATES	0.001 to 0.05
EUROPE	0.001 to 0.02

Mean Exposure Levels

TABLE 2. AIRBORNE FIBER IDENTIFICATION TEXTILE PLANT

(fibers per cubic centimeter)

	OPTICAL COUNT		RESPIRABLE FIBER		
Sample	Total	Respirable	NonGlass	Glass Optical	Glass SEM/EDX
1	.008	.008	.007	.001	ND
2	.054	.001	.001	ND	ND
3	.657	.651	.565	.086	ND

Representative Samples
ND = None Detected

ANIMAL STUDIES

Since textile fiber is too large to be respirable, most attention regarding health effects has been directed at glass wool. Special purpose wool fiberglass with a nominal product diameter less than one micron has been shown to cause cancerous tumors when administered in an artificial manner, such as by injecting the material into the trachea or surgically implanting it into the chest or abdominal cavity of animals. Even this very fine diameter wool fiberglass does not cause disease when inhaled (13) (14).

Textile fiberglass, such as used in composite reinforcement, has a much larger diameter. When textile fiberglass (continuous filament) was placed in the abdominal cavity of experimental animals, the incidence of tumor was indistinguishable from that seen in the controls (see Table 3) (11).

HUMAN STUDIES

There have been two epidemiologic studies which have investigated mortality due to lung cancer among workers engaged in the manufacture of man-made mineral fiber (MMMF) products, including continuous filament. Simonato, et al. (12) reported a standard morality ratio (SMR) of 97, using local comparisons. Similarly, Enterline(5) reported an SMR of 92, again using local comparisons. These SMR's do not support an association between employment in continuous filament production and lung cancer (see Table 4).

SUMMARY

In summary, textile, or as the Europeans refer to it, continuous filament glass fibers, have been evaluated for health effect by both human and animal exposure studies These studies have not demonstrated a cause and effect relationship between lung cancer and exposure to textile fiberglass. The material can cause a mechanical irritation. The uncured resin plastics in the composite system which the fiberglass is reinforcing can cause a sensitization type dermatitis which can be confused with the mechanical irritation caused by fiberglass. The airborne fiber concentration in textile manufacturing plants is low, and it is unlikely any of these fibers are respirable textile glass fibers.

The information contained in this paper should always be superseded by the manufacturers' Material Safety Data Sheets (MSDSs) and other safety and handling information provided by the individual manufacturers.

TABLE 3. INTRAPERITONEAL ADMINISTRATION GLASS FILAMENTS

	DIMENSIONS (microns)	DOSE (mg)	ANIMALS	TUMORS (malignant)
FILAMENT	L 50% <46 D 50% <7.4	40	47	1
GRANULAR GLASS (control)	-	40	45	2
SALINE (control)	-	-	45	2

Reported in series of studies - Pott, et al. 1987

TABLE 4. LUNG CANCER MORTALITY RATE (SMR)

	US	EUROPE	COMBINED
SMR	92	97	93
IN STUDY	3435	3566	7001
DEATHS	64	15	79

SMR Based On Local Comparisons

REFERENCES

(1) ANTONSSON, A. AND RUNMARK, S. (1987). Airborne Fibrous Glass and Dust Originating From Worked Reinforced Plastics. American Industrial Hygiene Association Journal, 48, 624-627.

(2) ASSUNCAO, J. AND CORN, M. (1975). The Effects of Milling on Diameters and Lengths of Fibrous Glass and Chrysotile Asbestos Fibers. American Industrial Hygiene Journal, November, 811-819.

(3) BOATMAN, E., COVERT, D., KALMAN, D., LUCHTEL, D. AND OMENN, G. (1988). Physical, Morphological, and Chemical Studies of Dusts Derived from the Machining of Composite-Epoxy Material. Environmental Research, 45, 242-255.

(4) DAHLQUIST, I., FREGERT, S. AND TRULSSON, L. (1979). Allergic Contact Dermatitis from Epoxy Resin Finished Glass Fiber. Contact Dermatitis 5, 190.

(5) ENTERLINE, P., MARSH, G., HENDERSON, V. AND CALLAHAN, C. (1987). Mortality Update of a Cohort of U.S. Man-Made Mineral Fibre Workers. The Annals of Occupational Hygiene 31, No. 4B, 625-656.

(6) ESMEN, N., CORN, M., HAMMAD, Y., WHITTIER, D. AND KOTSKO, N. (1979). Summary of Measurements of Employee Exposure to Airborne Dust and Fiber in Sixteen Facilities Producing Man-Made Mineral Fibers. American Industrial Hygiene Association Journal, 40, 108-117.

(7) KONZEN, J. (1987). Fiberglass and the Skin. In Occupational and Industrial Dermatology (Howard I. Maibach, ed.), Chapter 29, Second Edition. Year Book Medical Publishers, Inc., Chicago.

(8) KONZEN, J. (1988). Letter to Ms. Cathy Fehrenbacher at the U.S. Environmental Production Agency from Jon L. Konzen, M.D., of Owens-Corning Fiberglas Corporation, dated September 14, 1989, RE: Airborne Fibers at Textile Plants.

(9) KONZEN, J. (1988). Observations on Fiberglass in Relation to Health. In Occupational Medicine: Principles and Practical Applications (Carl Zenz, ed.), Second Edition, Chapter 67, Year Book Medical Publishers, Inc., Chicago.

(10) OTTERY, J., CHERRIE, J., DODGSON, J. AND HARRISON, G. (1984). A Summary Report on Environmental Conditions at 13 European MMMF Plants. In Biological Effects of Man-Made Mineral Fibres, Proceedings of a WHO/IARC Conference, Volume 1, 83-117.

(11) POTT, F., ZIEM, U., REIFFER, F., HUTH, F., ERNST, H AND MOHR, U. (1987). Carcinogenicity Studies on Fibres, Metal Compounds, and Some Other Dusts in Rats. Experimental Pathology 32, 129-152.

(12) SIMONATO, L., FLETCHER, A., CHERRIE, J., ANDERSEN, A., BERTAZZI, P., CHARNAY, N., CLAUDE, J., DODGSON, J., ESTEVE, J., FRENTZEL-BEYME, R., GARDNER, M., JENSEN, O., OLSEN, J., TEPPO, L., WINKELMANN, R., WESTERHOLM, P., WINTER, P., ZOCCHETTI, C. AND SARACCI, R. (1987). The International Agency for Research on Cancer Historical Cohort Study of MMMF Production Workers in Seven European Countries: Extension of the Follow-Up. The Annals of Occupational Hygiene 31, No. 4B, 603-623.

(13) SMITH, D., ORTIZ, W., ARCHULETA, R. AND JOHNSON, N. (1987) Long-Term Health Effects in Hamsters and Rats Exposed Chronically to Man-Made Vitreous Fibers. The Annals of Occupational Hygiene 31, No. 4B, 731-754.

(14) STANTON, M., LAYARD, M., TEGERIS, A., MILLER, E., MAY, M. AND KENT, E. (1977). Carcinogenicity of Fibrous Glass: Pleural Response in the Rat in Relation to Fiber Dimension. Journal of the National Cancer Institute 58, 587-603.

(15) WHO/IARC (1988) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans - Man-Made Mineral Fibres and Radon. Volume 43, IARC, Lyon, France.

INDUSTRIAL HYGIENE PROBLEMS ASSOCIATED WITH RECOGNITION AND ASSESSMENT OF EXPOSURE TO COMPOSITES

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ABSTRACT

Over 100 Boeing employees working with composites that are bonded with a phenol formaldehyde resin reported developing symptoms shortly after their resin was substituted for an epoxy compound.

Problems complicated by exposure at times to workplace temperature 90 to over 100° F along with significant overtime work involving seven days a week with one day off a month.

Industrial hygiene investigation stymied by present occupational health standards which do not appear adequate for some complex mixtures such as phenol formaldehyde resins. Excellent industrial hygiene practices were carried out when the use of the offending resin was cut back and then removed and ventilation added.

INTRODUCTION

Industrial hygienists play a most significant role in attempts to minimize the overall occurrence of adverse occupational health effects, including those likely to occur in the manufacture and use of composites. More often than not, the industrial hygienist is the first health professional contacted when workers develop problems. Unfortunately other occupational health professionals and management executives view industrial hygienists as operating exclusively in the areas of evaluation (monitoring) and control.

Graduate school degree programs for preparing professional industrial hygienists stress anticipation, recognition, evaluation and control of industrial health problems.

With a graduate degree or an appropriate undergraduate degree and one year of professional experience, the budding industrial hygienist is eligible to start on a program of certification administered by the American Board of Industrial Hygiene. The initial step involves successfully completing the Industrial Hygiene in Training exam. After four more years of professional experience a specialty examination must be successfully completed.

Specialties include the Comprehensive Practice (CP), Engineering (E), Chemistry (C), Acoustical Aspects (A), Air Pollution Aspect (AP), Radiological Aspect (R) and Toxicological Aspect (T). Persons certified in any of the above aspects may utilize the designation CIH. Industrial hygienists can be certified in more than one aspect.

The Comprehensive Practice specialist often serves in a capacity of a forensic scientist. The industrial hygienist is usually the first to be contacted when problems occur and may very well be the first health professional to visit the problem site. At that time information is obtained, workers are questioned, and monitoring may also be necessary. It may also be desirable to monitor at other times. When all of the available information has been assembled, reviewed, and digested, a report is prepared indicating the most probable source or sources of the health problems as well as recommendations for further evaluation if needed and methods for preventing future reoccurrences.

As a Comprehensive Practice Industrial Hygienist, the author's involvement in this problem began in September 1987 with a telephone call from a Boeing employee seeking information and assistance for health problems she was experiencing shortly after the epoxy resin used in a prepreg system was replaced by a new resin. She was a plastic bench mechanic who prepared prepreg panels for vacuum bag lay-up. She was under the impression that the new resin contained formaldehyde. Her symptoms included skin rash, headache, irritation of the eyes and upper respiratory tract along with memory lapse problems and fatigue.

Questioning indicated that she had contacted her supervisor who stated that there was no problem. She had not seen a Material Safety Data Sheet (MSDS), nor had she been provided health hazard information or training. She had contacted a union representative who was unaware of any problems.

She was advised to see a physician, preferably one experienced in occupational and/or environmental health problems and also to attempt to procure an appropriate MSDS to show to the physician. If the physician concluded that her symptoms were occupationally induced, then an industrial insurance claim should be filed. She was also informed that she could contact the consultant of the Industrial Hygiene and Safety Division, Washington State Department of Labor and Industries, who, after she completed an appropriate form, would conduct an investigation without divulging her identity if she so desired.

Shortly after this inquiry, a Boeing industrial hygienist was contacted and informed of the concerns as was the union. It was suggested to the union that a preliminary investigation be conducted in an attempt to learn the full extent of the problem an to obtain an MSDS.

Later the union did provide an MSDS and two prepreg samples. The MSDS indicated that the resin was of the phenol formaldehyde type. Analysis of the prepreg samples was conducted by the laboratory of the Department of Environmental Health for the presence of formaldehyde. Preliminary results indicated that the red backed prepreg yielded 700 μg of formaldehyde per gram of sample and the pink backed prepreg 1580 μg of formaldehyde per gram of sample. A gas chromatography/mass spectrophotometry analysis detected in decomposition products phenol and an unidentified organic compound exhibiting behavior like that of an organic acid. This information was reported to the union representative. Prepreg samples were later supplied by the Boeing Company.

The next association with this problem resulted from a telephone call in early summer from a reporter (Seattle Post Intelligencer) requesting information about possible exposures to phenolformaldehyde resins. He had previously been called by an employee who was concerned about how her situation was being handled. Later on Dr. Gordon Baker called indicating that he had examined some 50 patients working with Boeing who had developed various symptoms following the introduction of phenol formaldehyde resin in their shops. Dr. Baker is a Seattle area physician with an allergy practice. Since that initial call, the number of patients has increased to over 100.

GAS AND VAPOR EXPOSURES

Both the Washington State Department of Labor and Industries and the U.S. National Institute for Occupational Safety and Health (NIOSH) performed industrial hygiene investigations in the Boeing shops in question. The Department of Labor and Industries Investigations occurred on May 25, 1988 and June 6, 16, and 20, 1988. All contaminant results (Table 1) were well below their Permissible Exposure Limits (PEL).

Results of a NIOSH investigation conducted July 6 and 7 were reported in a correspondence to Mr. Ripley, Union Representative, Aerospace Machinists. Formaldehyde concentrations ranged from nondetectable to a high of 0.073 mg/m^3. The WISHA limit for formaldehyde is 1.2 mg/m^3(1 ppm) as a time-weighted average with 2.4 mg/m^3 (2 ppm) as a

TABLE 1

SUMMARY OF WISHA MONITORING RESULTS

Contaminant	No. of Samples Building No. 2	No. of Samples Building No. 4	Sample Results Building No. 2	Sample Results Building No. 4	WISHA PEL
5-25-88					
Formaldehyde	4	0	0.004 ppm (TWA)		1 ppm-TWA
			0.004-0.073 ppm (STEL)		2 ppm STEL
Phenol	4	0	< 0.01-0.04 ppm		5 ppm
6-9,16,20-88					
Formaldehyde	10	6	0.01-0.03 ppm	<0.08 ppm	1 ppm TWA
					2 ppm STEL
Phenol	9	0	0.001-0.5 ppm	-	5 ppm
Acetone	4	4	2.3-7.6 ppm	< 1 ppm	750 ppm
Methylene Chloride	2	4	0.1 ppm	< 1 ppm	100 ppm
Styrene	2	4	1.2 ppm	< 1 ppm	100 ppm
Antimony Trioxide	4	0	<0.01 mg/m^3	-	0.5 mg/m^3
Amines	0	2	-	< 0.2 ppm	1 ppm
n-hexene	0	4		< 1 ppm	50 ppm
Total particulates	4	0	0.48-1.1 mg/m^3-	10 mg/m^3	

TABLE 2

SYMPTONS REPORTED BY THE STATE HEALTH DEPARTMENT EXPERIENCED BY EMPLOYEES:

24	headache	10	diarrhea
21	irritation of eyes	9	cough
19	irritated throat	8	muscle aches and pains
18	nausea	7	burning in nose
16	dizziness	6	fatigue
11	tearing of eyes	6	dark urine
10	chest tightness	5	rashes

Short Time Exposure Limit (STEL). NIOSH on the other hand utilizes an occupational standard for formaldehyde of Lowest Feasible Limit (LFL).

Three atmospheric samples analyzed by GC/MS contained various C9 - C12 alkanes plus C9 - C10 aromatics such as trimethylbenzenes and diethylbenzenes. One sample contained formaldehyde and an unknown, probably an alcohol/ether compound.

Bulk sample results analyzed at different temperatures by GC/MS identified compounds including formaldehyde, etnanol, isopropanol, phenol, salicylaldehyde, MIBK, ethyl acetate, toluene, MEK and several compounds not identified. These included a couple of alcohol/ether type compounds and a series of higher boiling phenyl compounds.

NIOSH also performed a Health Hazard Investigation (Report pending).

Industrial hygienists of the Boeing Company have also performed extensive monitoring.

None of these investigations turned up results that were in violation of any state standards.

Unfortunately some general atmospheric techniques utilized to assess potential health hazards of worker exposed to toxic chemicals are relatively ineffective. This is especially true for complex mixtures involving resin formulations, some of which have been developed for use in composites.

A number of technical difficulties are apparent. In many instances all resin by-products have not been identified, and if identified, information on toxicity may well be absent. Two examples follow:

Example 1.

In mid-1982 an administrator of a state agency requested assistance from the Field Response Team to determine if possible the source or sources of symptoms experienced by staff members immediately after a carpet had been installed. The carpet was installed on a weekend with an adhesive. On Monday, what was described as a "very offensive" odor was discernable by all employees. Beginning on Tuesday and continuing for 3 weeks. Twenty of 35 employees were absent from work with time lost ranging from one hour to a maximum of 14 days. Total lost time amounted to 521 hours.

When inquired about what made symptoms better, 18 stated staying away from office while 25 indicated that staying in the office made symptoms worse. The carpet company and the adhesive company both reported by telephone that bonding agents were styrene-butadiene-latex resins. Atmospheric monitoring did not reveal the presence of any contaminants in amounts likely to constitute a substantial health hazard when compared with present standards. Analysis of a bulk sample indicated a total chromatogram of 68 peaks representative of a petroleum based solvent mixture.

When reviewed individually, concentrations of contaminants did not explain the reported health problems.

In 1984, University of Arizona (Van Ert et al., 1985) staff members discovered a common prominent emission product from three carpet samples. That contaminant was 4-phenylcyclohexene resulting from the styrene-butadiene-latex compounds used to bond carpet fibers to the backing.

Since 4-phenylcyclohexene was not commercially available, it was necessary to synthesize it for further research. Results of that preliminary research indicated that it does not appear to be a skin or eye irritant. Pulmonary tissue response was evaluated by injecting 2 μL of 4-phenylcyclohexene into the surgically exposed trachea of four rats. At the end of 15 days the animals were sacrificed and examined. Hemorrhaging was noted within the lungs of two of the four rats. The bronchioles were primarily impacted and lactate dehydrogenase from lung lavage was elevated approximately 400 percent suggesting cellular damage.

Example 2.

Researchers in Sweden (Bruze et al., 1987) reported isolating a number contact sensitizer in resins based on phenol formaldehyde. Prior to this series of studies, only four sensitizers were recognized in phenol formaldehyde compounds including 2-methyl phenol, 4-methyl phenol, 2,3,6-trimethyl phenol and formaldehyde. Eleven new contact sensitizers were isolated utilizing guinea pigs and humans. This study did not examine the possible effects of respiratory exposures.

The above examples reinforce the conclusion that there is still a great deal to learn about resin mixtures and by-products.

Exposure to Fibers and Non-Fiber Particles

In addition to monitoring for gases and vapors, the State of Washington industrial hygienists also monitored for the presence of fibers and dust. Results (Table 1) reported total particulates ranging from 0.48 mg/m^3 to 1.1 mg/m^3. Scanning Electron Microscopy (SEM) indicated that glass fibers were observed.

Man-made mineral fibers are considered to be potentially carcinogenic when these fibers possess the same diameter and length-to-diameter ratio as asbestos fibers. A SOHIO MSDS for Fiberfrax, a ceramic fiber, includes the following:

Product Hazard Summary

Health Warning!

MAY BE HARMFUL IF SWALLOWED
MAY BE IRRITATING TO SKIN, EYES, AND RESPIRATORY TRACT POSSIBLE CANCER HAZARD BASED ON TESTS WITH LABORATORY ANIMALS

Respiratory Protection

Use NIOSH or MSHA approved equipment when airborne exposure limits are exceeded. NIOSH/MSHA approved breathing equipment may be required for non-routine and emergency use. Ventilation may be used to control or reduce airborne concentrations. Acceptable respirators recommended for airborne ceramic fiber concentrations exceeding 2 fibers/cc are:

Concentration	Respirator Type
2.0-5.0 f/cc	3M 8710 or equivalent
5.0-50.0 f/cc	Survivair full face piece with high efficiency filter 1090-00 or equivalent
> 50.0 f/cc	MSA 01-00-06 full face piece type C supplied-air or equivalent. OSHA approved air source required

Pending the results of long-term health effects studies, engineering control of airborne fibers to the lowest levels attainable is advised.

Hazardous Ingredients/Identity Information

Ingredient	CAS number	OSHA PEL	ACG-IHTLV-TWA
Petroleum Process Oil	64742-30-9	5 mg/m^3 oil mist	5 mg/m^3 oil mist
Mineral Wool Fiber	None total dust	15 mg/m^3 total dust	10 mg/m^3
(Nuisance Particulates)		5 mg/m^3 respirable fraction	

Health Hazard Data

Primary Routes of Entry: Inhalation, Skin and Eye Contact

Acute: Mineral wool fiber and other nuisance particulates may cause transitory skin irritation (itching) and possible irritation of eyes and upper respiratory tract.

Chronic: The World Health Organization's International Agency for Research on Cancer (IARC) has classified mineral wool as Group 2B, "possibly carcinogenic to humans". Based on studies in which mineral wool was injected or implanted in laboratory animals (artificial means of exposure), IARC concluded there was limited evidence of cancer in animals. This classification did not consider the lack of cancer in animals exposed by inhalation, the normal means of exposure.

Based on some epidemiologic studies, IARC concluded there was limited evidence of an association between mineral wool and cancer in production workers.

100 percent concentration of petroleum process oil has been shown to be a carcinogen on the skin of laboratory animals in the absence of normal hygiene over a two year period.

Carcinogenicity: NTP - NO IARC - 2B OSHA - NO

Medical Conditions Aggravated by Exposure: Any condition which may be aggravated by mechanical irritants.

Information on the bag containing Certainteed Kraft Faced Roll of fiber glass states.

CAUTION

This fiber glass wool insulation may cause skin, eye and respiratory irritation. Based largely on experiments in which laboratory animals were exposed artificially to glass fibers by injection or surgical implantation, fiber glass wool has been classified as possibly carcinogenic to humans. When handling and/or applying insulation:

- Wear long sleeves, gloves and cap.
- Wear eye protection (goggles, safety glasses or face mask).
- A NIOSH/MSHA approved dust respirator such as a 3M model #8710 or #9900, or equivalent, should be used.

After handling and/or applying this insulation:

- Bathe with soap and warm water
- Wash work clothes separately and rinse washer after use.

For additional product safety information, including dust respirator data and material safety data sheets (MSDS), call (215) 341-7000.

Contains some fibrous glass dust, urea, polymer with formaldehyde, phenol and asphalt.

The time is ripe to update occupational health standards for man-made mineral fibers. These substances can no longer be considered nuisances. A number of producers already use lower standards.

A further complicating factor concerns exposure to man-made mineral fibers and dust particles that have resin residues or other contaminants attached. Need to determine if those attached compounds increase the health hazard potential due to skin contact and inhalation.

Other Environmental Factors

Metabolic job requirements, temperature condition and increased working hours could well have an additional influence on worker health. Increases in temperature and metabolic job requirements could result in discomfort and more important heat stress. Increased

breathing rates will also increase the amount of contaminants inhaled. Add significant overtime to the above, and the results could be drastic.

When questioning some of the employees about their work environments, it was mentioned that building 1702 was a wooden structure constructed during World War II for use as cold storage for cadavers. This building was void of adequate ventilation and workers reported temperatures of over 100° at times in the summer.

Employees also mentioned that they were required to work seven 8-hour days a week with one day off a month. Some mentioned working seven 10-hour days, and one individual indicated that he only had one day off every two months.

As mentioned previously, Dr. Baker has over 100 patients who work for Boeing, most with composites. Of 41 identified as working in building 1702, 9 were males and 32 females. Symptoms include:

TABLE 3

SYMPTOMS - BUILDING 1702 DR. BAKER'S PATIENTS

Symptoms	Number	%	Symptoms	Number	%
Eye irritation	31	76	Diarrhea	11	27
Upper respiratory irritation	35	85	Dizziness	22	54
Skin rash	18	44	Shortness of breath	24	59
Cough/wheeze	23	56			
Headache	32	78	Fatigue	34	83
Nose bleeds	11	27	Irritability	32	78
Blood in urine	5	12	Depression	28	68
Nausea	11	27	Memory lapse	30	73
Chest pains	20	49	Loss of sex drive	17	41
Personality change	27	66	Other 3-Menstrual problems 2-joint pains		

Total number examined, 41: 9 males, 32 females

In addition to a physical exam, some or all of the following tests were performed.

TABLE 4

TESTS ON DR. BAKER'S PATIENTS ANTIBODY ASSAY LABORATORIES

Lymphocyte Surface Markers

- Total T Cells
- Total B Cells
- T Helper Cells
- T Suppressor Cells
- IL2 Receptor Cells
- Ta1 Positive Cells
- H/S Ratio

IL1 Production by monocytes

Autoantibody screen

- Antinucleal antibody
- Antimitochondrial antibody
- Antosmooth muscles antibody
- Antiparietal antibody
- Antibrush border antibody

Antibodies to:

Formaldehyde	IgE	IgG	IgM
Trimellitic anhydride	"	"	"
Isocyanates	"	"	"

Antibody assay laboratories provides the following information with references upon request to users and nonusers of their service.

BIOLOGICAL MONITORING FOR IMMUNE DAMAGE DUE TO XENOBIOTICS
ALAN BROUGHTON M.D. AND JACK D. THRASHER PhD

Monitoring the health risks of environmental hazards includes:

a) Ambient Monitoring: Assesses the health risks by measuring the external exposure to the chemical.

b) Biological Monitoring of exposure: Assesses the health risk by evaluating the internal doses.

c) Biological Monitoring of effects: This aims at identifying individuals with signs of adverse health effects e.g., increase in hepatic enzymes in cases of exposure to hepatotoxic chemicals or proteinuria in the case of nephrotoxic chemicals.

Rapid increases in our knowledge, and the increasing availability of tools to monitor the immune system, have permitted the development of biological monitoring of effects on the immune system.

EFFECTS OF CHEMICALS ON THE IMMUNE SYSTEM.

Until recently it was the generally accepted view that certain chemicals affect the immune system by inducing a state of allergy or hypersensitivity in the patient. This often resulted in the production of asthma (TMA and reactive dyes) or skin hypersensitivity (formaldehyde).

More recently other effects have been noted; these include the production of immunological lung disease (silicosis, berylliosis, and farmers lung), activation of the macrophages by insecticides (malathion), and the demonstration of immunosuppression by dioxin.

We have recently demonstrated indices of immune activation in patients exposed to low levels of formaldehyde, trimellitic anhydride, and toluene diisocyanate, as well as Chlordane (acute and chronic exposure), trichloroethylene and perchloroethylene. The parameters of immune activation are the presence of activation markers (Ta1) on the T lymphocytes and the appearance of autoantibodies to a variety of tissues.

We have also observed that in acute exposure there is an increased production of interleukin 1 by the macrophages and in chronic exposures a reduction of interleukin 1 production. The mechanisms involved are unclear, but the following working hypothesis is worthy of note.

Xenobiotics undergo metabolism by the liver, usually using the cytochrome p450 enzyme system, often producing highly reactive chemicals such as epoxides as intermediaries before final water-soluble excretory compounds. These epoxides are capable of damaging local cells and exposing autoantigens and the activation of the immune system with the production of the Ta1 cells marker.

The epoxides also activate the phagocytosing macrophages, which results in the in vitro production of increased amounts of interleukin 1. Further exposure results either in an inability of the macrophage to respond, or the production of interleukin 1 inhibitors such as prostaglandins.

Once this cycle of events has started, continued exposure to the primary compound results in further immune activation through autoantibody production. Indeed, the activation may occur through additional chemicals producing what has been called the "chemical hypersensitivity syndrome."

The symptoms of this controversial syndrome are vague but can be, on careful history- taking related back to an episode of a "flu" like illness from which the patient never really recovered. The patient then develops an inability to cope with many of the situations produced by twentieth century living; they complain of symptoms in new buildings, new cars, diesel fumes, perfumes, and many other chemicals, which affect some patients to the point of withdrawing from modern society.

Some chemicals (formaldehyde, TMA, TDI, and reactive dyes) combine with human serum albumin on exposure and illicit the production of antibodies. These antibodies are sometimes IgE and produce systems of classical allergy (e.g., asthma); other times they produce IgG or IgM, which can be used as an index of exposure.

LABORATORY TEST AVAILABLE AND RECOMMENDED FOR BIOLOGICAL MONITORING FOR HEALTH EFFECTS

Antibody Assay Laboratories has, following two years of research into this problem, selected protocols covered in Table IV to establish the presence of immunological damage in individuals exposed to low-level xenobiotics.

One of the more significant contaminants from the viewpoint of neurobehavioral aspect is formaldehyde. Neurobehavioral manifestations were reported in two groups of histotechnology technicians exposed to formaldehyde and solvents in the preparation of human and animal tissue for examinations. In one investigation, 420 technicians were surveyed to determine possible adverse health effects (Kilburn et al., 1983). Formaldehyde concentrations of 0.4 of over 5.0 ppm were obtained during a short check of tissue preparation. Findings included perceived impairment of memory, mood, balance, and sleep, together with additional neurobehavioral symptoms frequently associated with formaldehyde in other studies.

The second study involved 76 histology technicians (Kilburn, et al., 1985) along with a control group of 56 secretaries and clerks, all from the same hospital. The technicians were found to suffer greater frequencies of lack of concentration, loss of memory and disturbed sleep.

Two groups of formaldehyde-exposed male employees (Kilburn, Warshaw, et al., 1985) were compared with a control group of 26 unexposed male hospital workers. Forty-five male fiberglass batt producers averaged combined frequencies of neurobehavioral, respiratory and dermatological symptoms of 17.3 and 10.7 for hot and cold work areas

respectively. Eighteen male histology technicians averaged 7.3 combined frequencies for the above mentioned symptoms while the 26 controls averaged 4.8.

Neurobehavioral symptoms included sleep disturbances, insomnia involving difficulty in falling asleep, frequent waking and sleeping for only a few hours. These symptoms along with concentration loss, recent and remote memory loss, instability of mood and irritability were all increased with exposure.

DISCUSSION

The PEL occupational health limit for formaldehyde is 1.0 ppm based on an eight-hour time-weighted average along with a Short-Term Exposure Limit (STEL) of 2.0 ppm. While atmospheric concentrations of formaldehyde in Building 1702 were low, hours of exposure of some ranged from 56 to 70 hours/week. It is also well to keep in mind that occupational health standards were not developed to protect all exposed workers. Individual sensitivity is critical. These standards are also based on a 40-hour workweek. In addition, epidemiologic data utilized in the development of occupational health standards was obtained primarily from studies invoiving white males. Finally, a major drawback is associated with the effectiveness of both monitoring and analytical techniques employed in assessing atmospheric environments involving complex mixtures. No one absorbent will likely collect all contaminants, nor will the most sophisticated analytical methods identify all of the compounds detected.

FACTS AVAILABLE

1. Symptoms--Reported After Introduction of Phenol Formaldehyde
2. Complex Mixture--Many By-Products--Some Not Identified.
3. Similar Problems With Other Complex Mixtures--Ex Styrene--Butadiene--Latex in Carpets
4. Formaldehyde's Potential for Neurobehavioral Effects--Present in Low Concentrations --Extended Work Periods.
5. Epidemiological Data Based on White Males
6. Work Shifts: 8 hours/day, 7 days/week, 1 day off/month
7. PELs Based on 8 hours/day--40 hours/week Not Designed to Protect All Workers

8. Some Work Areas--Poor Ventilation--Discomfort--Heat Stress

9. Skin Contact--No Gloves Immediately Difficult to Work with Gloves

10. Workers--Reluctant to Report Health Problems

11. Phenol Formaldehyde Resin Removed--Ventilation Added--Health Problems Reduced.

CONCLUSIONS

The most probable cause of the symptoms reported by composite workers resulted from exposure to phenol formaldehyde resin and resin by-products plus extended work periods along with the addition of discomfort and possible heat stress.

REFERENCES

Bruze, M., Contact Sensitizers in Resins Based on Phenol and Formaldehyde, Acta Dermato-Venereologica, Supplementum 119, Department of Occupational Dermatology, Department of Dermatology, University of Lund, Lund, Sweden, 1985.

Kilburn, K.H., Warshaw, R., Boylen, C.T., Biames, I., Johnson, S., Seidman, B.C., DeFlorio, G., Toxic Effects of Formaldehyde and Solvent in Histology Technicians, J. of Histotech, 6:2, June 1983, pp. 73-76.

Kilburn, K.H., Seidman, B.C., Warshaw, R., Neurobehavioral and Respiratory Symptoms of Formaldehyde and Xylene Exposure in Histology Technicians, Arch. of Env. Health, 40: 4 1985, pp. 229-233.

Kilburn, K.H., Warshaw, R., Boylen, C.T., Johnson, S., Seidman, B., Sinclair, R., Takaro, T., Pulmonary and Neurobehavioral Effects of Formaldehyde Exposures, Arch. of Env. Health, 40: 5, 1985, pp. 254-260.

Van Ert, M.D. Clayton, J.V., Crabb, C.L., and Walsh, D.W., Identification of Characteristics of and phenylcyclohexene on Emission Product from New Carpeting, University of Arizona, College of Pharmacy, Department of Pharmacology and Toxicology, Tucson, Arizona, 85721, (1-8-87).

EXPOSURE EVALUATION OF COMPOSITE MATERIALS WITH EMPHASIS ON CURED COMPOSITE DUST

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ABSTRACT

Composites have been used widely in numerous applications across the manufacturing industry. The resin as well as fiber composition of these materials varies with the application. Employee exposure evaluations of composites must consider such factors as the differences between product component availability under uncured vs cured conditions, the component specific toxicity, the relative rate of transdermal penetration, and methods utilized to control employee contact or exposure. Several methods are available to determine component availability and dermal penetration characteristics.

Various monitoring techniques can be employed to predict exposure to composites. Air monitoring, surface contamination testing, biological monitoring and product analysis all produce information which may be useful in a hazard assessment. Also, in vitro dermal penetration testing provides valuable information on the significance of the dermal route of exposure.

We report on the implications of research conducted to supplement our information base on the potential health effects of composite materials. Dust produced by machining cured composite have been subjected to morphological, chemical, and toxicological tests. These studies have provided information useful in estimating relative insult of dust to lung tissue. Additionally, the tests provide a method to screen various resin/fiber combinations. Data from our studies of several resin and fiber combinations suggest that differences noted in relative cytotoxicity and lung insult cannot be explained by resin or fabric type. Toxicity data for aluminum oxide, quartz and composite dust were evaluated to estimate a mg/m^3 index threshold level for exposure to composite dust. An air concentration in the lower mg/m^3 range appears to be predictive of a threshold level. Presently used local ventilation is considered acceptable for restricting exposure to levels below the predictive threshold.

Future research in the areas of development and use of novel monitoring methods, toxicity testing and chemical dermal penetration measurements will provide useful information to health professionals performing composite exposure evaluations. Also, research should continue on combining tool design criteria with ventilation requirements for machining processes involving composite materials.

INTRODUCTION

Major material changes have occurred in the aerospace industry with the introduction and adoption of advanced composites to replace metallic as well as other types of materials. Although the introduction of new types of composite component resins and raw fibers provides challenges for the health and safety community, there is a long history of experience with the general class of composites in the form of fiberglass-epoxy materials which have been used in various applications for several decades. What we have witnessed recently is the growth of composites technology to include introduction of both new fabrics as well as the resin portions of the composite. Additionally, both thermoset and thermoplastic preimpregnated systems are being proposed for a greater number of applications. Many of the components of the preimpregnated systems, as well as the final products they represent, are lacking extensive toxicity evaluation (Kowalska, 1982). However, it is not clear that this is a function of the new technology or simply a symptom of a more general issue, which is the general lack of toxicology information on the entire spectrum of industrial chemicals.

The purpose of this paper is to first outline the general considerations in evaluating the hazard of composite materials. These include defining the route of exposure for a particular work operation, and identifying the applicable monitoring methods used to determine the extent of exposure. An example is presented of how dermal penetration data combined with toxicology information can be used to estimate relative hazard of chemicals within a group. The second purpose of the paper is to integrate the results of research on morphological, chemical and animal toxicology characteristics of graphite dust with existing information to provide an estimate of the potential health effects and acceptable exposure thresholds.

The composite dust research data analyses is based on the results of a Boeing sponsored research project conducted by an interdisciplinary research team at the Department of Environmental Health, University of Washington. This research is reported in a series of three papers published in the journal Environmental Research.

METHODS

Exposure Considerations: In Vitro Penetration Methods

Methods for experimental determination of in vitro penetration of industrial chemicals using the hairless mouse are detailed elsewhere (Bronaugh and Maibach, 1985), as is the background for exposure calculations utilizing the dermal data (Bourcier, 1986). Penetration data combined with toxicology information made it possible to generate relative hazard indices for groups of chemicals exhibiting a similar mechanism of toxic effects.

Graphite Dust Studies

Morphological Evaluations. Light and electron microscopy evaluations of six different types of composite dust were performed in order to characterize the materials as to size distribution of both bulk and fractionated materials.

A listing of the six product types and representative operations appears in Table 1. Specific information on the dust collection, fractionation, and analysis methods is provided in the research group's report (Boatman, 1988).

Chemical Evaluations. Composite dust materials were subjected to thermal gravimetric analysis and gas chromatography/mass spectrometry measurements of thermal degradation products. Methods are detailed elsewhere (Boatman, 1988).

Toxicological Studies. Fractionated composite dust samples, as well as quartz and aluminum oxide comparison controls, were subjected to cytotoxicity testing utilizing isolated rabbit lung macrophage system. In vivo investigations of the same dust types were conducted in pathogen-free rats. Dust was administered intratracheally and animals sacrificed one month later for pathological examination of lung tissue. Tissue sections were rated based on the following indices: 0, no pathology evident; 1, little or seemingly incidental pathology; 2, some definite pathological features noted; 3, moderate degree of pathology; and 4, marked or severe pathological changes. A complete description of study methods is presented elsewhere (Luchtel, 1989; Martin, 1989).

TABLE 1

DESCRIPTION OF COMPOSITE DUST TEST MATERIALS AND OPERATIONS.

Sample #	Material and Fabric Type	Matrix[a] Composition	Trimming Operation
1	Graphite[b]	PEEK[c]	Spindle shaper: 10,000 RPM
2	Fiberglass	Epoxy + amine curing agent[f]	Spindle shaper: 3,450 RPM
3	Graphite-PAN\ Kevlar®	Epoxy + amine curing agent[f]	Hand Router: 23,000 RPM Saber saw Spindle shaper: 3,450 RPM
4	Graphite-PAN[d] curing agent[g]	Epoxy + aromatic amine	Hand router: 23,000 RPM
5	Graphite-Pitch[e] curing agent[g]	Epoxy + aromatic amine	Spindle shaper: 3,450 RPM
6	Graphite-PAN agent[h]	Epoxy + amine curing	Hand router: 23,000 RPM

[a] Exact chemical composition of matrix is proprietary
[b] Proprietary fabric type
[c] Non-epoxy polyetheretherketone thermoplastic
[d] Abbreviation for Polyacrylonitrile graphite precursor
[e] Pitch graphite precursor
[f] Two products having similar epoxy and curing agent chemical composition.
[g] Two products having similar epoxy and curing agent chemical composition.
[h] Contains polybutadiene compound

Note: All systems are preimpregnated, i.e., resin impregnation of bundled continuous filaments to form a continuous tape or fabric which is later plied in layers of the same or different alignments.

RESULTS AND DISCUSSION - EXPOSURE EVALUATION OF COMPOSITE MATERIALS

Material Source, Work Operation, and Route of Exposure

Several factors must be considered in exposure evaluation of composite materials or any industrial product. Probably the most obvious to the health professional is the difference between uncured and cured materials. Uncured systems can occur in the form of manually

impregnated and preimpregnated fabric. A general listing of various operations by sources and routes of exposure is presented in Table 2.

It is noted that the major routes of exposure to composites involve both dermal and inhalation while the source of exposure varies with the different work operations. For example, layup operations are associated with potential inhalation of resin vapors and skin exposure to uncured resins while machining of parts is associated with potential skin and inhalation exposure to composite dust.

Exposure Level/Body Burden

Several techniques can be employed to estimate the potential level of exposure produced by an airborne chemical or one which is in contact with skin (Table 3). The utility of any technique method in defining exposure is dependent on the validity of the method as an indicator and the type of information. For example, personal air monitoring may be a good indicator of inhalation exposure but a poor indicator of total exposure if the chemical of interest is in contact with the skin and absorbed well. Oftentimes several monitoring tools are used in combination to paint a full picture of the exposure scenario. Biological monitoring is used to measure the body burden affected by exposure and may be a more direct link to health effects than is personal monitoring (Lauwerys, 1983). Biological monitoring works best when the relationship between the level of chemical, metabolite or other parameter in some biological media and the degree of adverse effect is firmly established.

Significance of Absorption Rate in Comparing Relative Hazard

The rate of absorption of chemicals into the body is a parameter utilized to estimate the amount of chemical which is capable of being absorbed per unit time. In the case of dermal permeation it indicates the relative significance of the dermal route as a mode of entry.

Some chemicals having low vapor pressures may not present a hazard in terms of inhalation exposure, yet may be absorbed well through the skin as mentioned above (example: ethylene glycol monomethyl ether and ethylene glycol monoethyl ether and their acetates). Therefore, airborne monitoring alone may underestimate total exposure.

TABLE 2

LISTING OF EXPOSURE ROUTES BY COMPOSITE MATERIALS AND OPERATIONS

Composite Type/Cure	Operation	Exposure Route/Source[a]							
		Inhalation					Skin		
		IURV	IRF	IURD	ICCD	ITDP	SCUR	SCRF	SCCD
Uncured Resin and Cloth	Tooling	X	X		X			X	
	Sand/Fill, Rework	X	X					X	
Uncured Prepreg	Kitting	X		X			X		
	Layup,	X		X			X		
	Bagging	X					X		
Cured Composite	Debagging,					X			
	Trim, Machining,				X	X			X
	Assembly				X				X

[a] Route/source are IURV, Inhalation/uncured resin vapors; IRF, inhalation/resin fibers; IURD, inhalation/uncured resin dust; ICCD, inhalation/cured composite dust; ITDP, inhalation/composite thermal decomposition products; SCUR, skin contact/uncured resin; SCRF, skin contact/raw fiber; SCCD, skin contact/cured dust.

TABLE 3

VARIOUS METHODS USED TO DEFINE CHEMICAL EXPOSURE

Type of Monitoring	Function
Personal monitoring	Determine component air conc. at breathing zone
Area air monitoring	Determine air conc. in general work environment
Wipe testing	Determine surface contamination as indicator of chemical availability
Chemical analysis	Determine/verify product components/contaminants
Thermogravimetric analysis	Determine thermal stability
Chem. analysis of off-gassed materials over a wide temperature range	Identify and quantify product component, contaminant, and decomposition by-products
Biological monitoring	Determine level of parameter in biological media associated with adverse effect/exposure level

Dermal absorption rates can be measured in vitro as well as in vivo in animal models which have been developed for this purpose (Bartek et al., 1983; Bronaugh and Maibach, 1985). Dermal penetration rates may be combined with toxicology data to compare members of a class of chemicals (Bourcier et al., 1986). To illustrate this we consider the comparison of chemical-1 and reference chemical-2, two potential components from the same chemical class but with different dermal absorption rates and potencies (similar mechanism of action). The Relative Hazard Index (RHI) of chemical-1 with respect to reference chemical-2 takes into

account the differences in both permeation rate and toxicity (Threshold Limit Value, or TLV, as a measure of relative toxicity) as presented below:

$$RHI = \frac{RPR}{RTLV}$$

Where: RPR = Ratio of permeation rates of chemical-1 to chemical-2 and;

RTLV = Ratio of the Threshold Limit Value of chemical-1 to that of chemical-2 .

Therefore, an RHI greater than 1.0 indicates a greater hazard attributed to chemical-1 over the reference chemical-2. This method has been developed for use in evaluating relative hazard of several organophosphate insecticides using methyl parathion as the reference chemical (Bourcier et al., 1986). The same procedure can be used in hazard evaluation of other classes of industrial chemicals including composite components.

Consideration of Potential Adverse Effects of Composite Materials - Composite Dust

Composite materials can contain a number of different chemical components of diverse toxic endpoints. Specific composite chemicals and their toxic effects have been reviewed in detail in an earlier paper and therefore will not be covered here. Consideration of the type of adverse effect associated with a chemical and the potency of the effect is probably the most fundamental information required for hazard evaluation.

Toxicology information can be derived from animal studies, epidemiological investigations, or can be extrapolated from comparisons of chemicals with similar structure or chemical properties. In many cases, toxicology data may be somewhat limited and studies are initiated to fill the information gaps. Composite dust provide a good example of a material for which there was a general lack of information on morphological, chemical and toxicologic properties.

Several questions have been raised regarding the potential hazards of composite material dust. Are they basically particulate dust or fibers? Does the material retain the chemical reactivity of the epoxy components even after cure? Are they biologically inert?

How are potential exposures to these materials to be evaluated? What types of industrial hygiene or engineering controls, if any, are recommended?

In the past, several of these questions were answered utilizing the data available from studies on only the individual components of the composite, such as cured epoxy dust, graphite dust, and fiberglass, rather than the composite as a whole. Additional information was needed to extend the knowledge base to include newer materials used in the aerospace industry.

Morphology - Chemistry Studies. A summary of pertinent results of the morphology and chemistry portion of the research is presented below in Table 4. Detailed treatment of the data is found elsewhere (Boatman et al., 1988).

The results of the morphological/chemical studies suggest that the polymeric dust is lower in desorbable and/or reactive decomposition product loading than most other plastic products and that exposure to significant amounts of decomposition products during milling, machining, and drilling processes is not likely to occur. The data also indicate that the various composite materials would be expected to be quite durable (stable) when in contact with lung tissue. This may have some significance when studying the mechanism of action of the dust when deposited in the lung as well as their disposition. With fibers, it has been proposed that those fibers of greater durability (combined with other characteristics such as small diameter) are more prone to production of scarring of lung tissue than are those of low durability. Therefore, the mechanism of action of these materials in the lung may be characterized as not involving a direct chemical insult.

When we consider that the bulk dust is particulate in nature with few fibers, the durability of the material becomes more difficult to evaluate. In the case of mineral particulate material, the actual form of the dust (crystalline vs non-crystalline) seems to have the greatest impact on the fibrotic response in lung tissue.

Toxicology Studies. The results of the in vitro chromium-51 cell viability studies and in vivo intratracheal injection studies are presented in Figure 1. Representations of the same data by composite component type are presented in Tables 5 and 6.

In the in vitro investigation the level of chromium-51 release from alveolar macrophage cells after incubation for 48 hours was used as an indicator of cell death. As expected, the quartz sample (Q) produced marked cytotoxicity whereas the aluminum oxide release was similar to that of the control media. The composite samples produced cytotoxicity

TABLE 4

RESULTS SUMMARY OF MORPHOLOGICAL/CHEMICAL STUDIES

Area of Study	Findings
Morphology	Analysis of bulk materials revealed particulate with limited fiber composition and few percent of total defined as respirable. Size fractionated dust indicated variation among materials but all were within size range necessary for deposition to alveolar region of lung.
Chemistry	Composite materials were chemically and thermally stable Thermal decomposition analysis at temperature > 250° C indicated relatively low yield but wide variety of chemical species

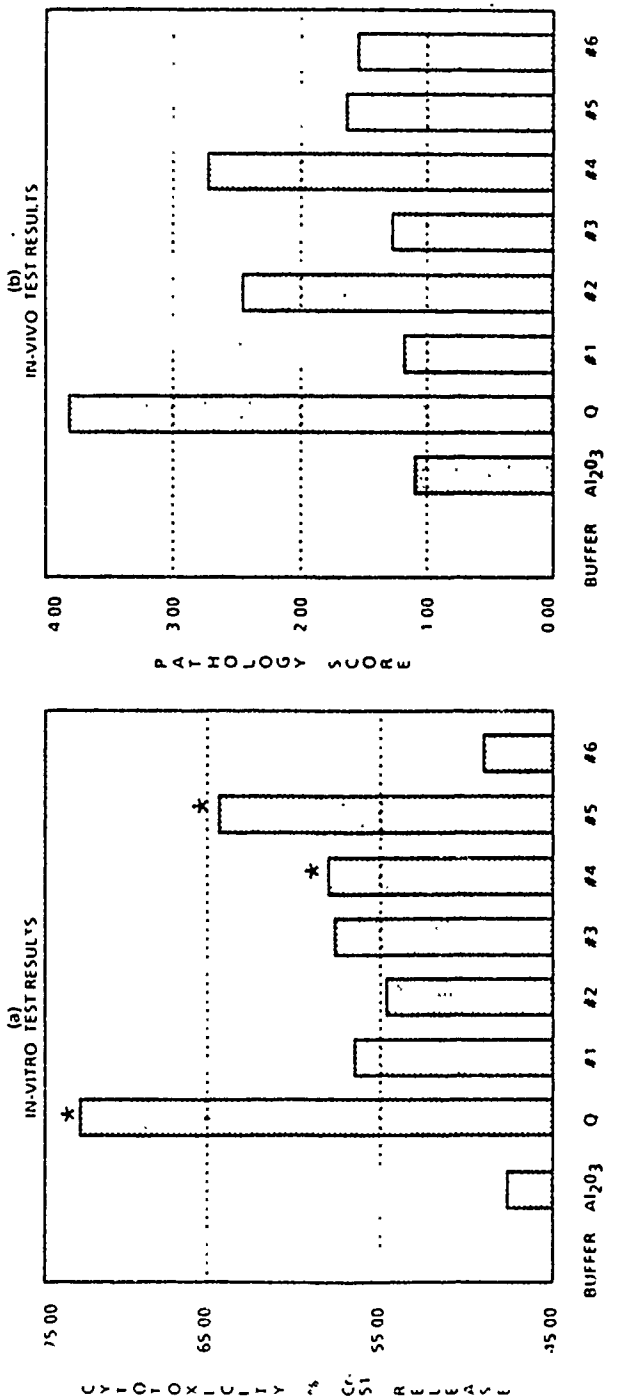

Figure 1. Comparison of in vitro and in vivo results of toxicological studies of composite dust. (a) in vitro data, * indicates significant difference when compared to Al_2O_3 control. ($p = 0.05$) using Dunnett's t-test; (b) in vivo data.

TABLE 5

COMPONENT SPECIFIC RESULTS: IN VITRO STUDIES

	Chromium-51 Release/Resin system			
Fabric	EA[a]	EA_1[a]	EAA	PEEK
Fiberglass	54(2)[b]	-	-	-
Graphite PAN/Kevlar®	57(3)	-	-	-
Graphite PAN		49(6)	57(4)*	-
Graphite-Pitch			64(5)*	-
Graphite-unknown				56(1)

[a] Polybutadiene containing resin.
[b] ( ) indicates sample number.
* statistical difference when compared to Al_2O_3 control ($p = 0.05$) using Dunnett's t-test.
Note: Resin systems are EA- Epoxy/amine; EA_1- Epoxy/amine-1; EAA-Epoxy/aromatic amine.

TABLE 6

COMPONENT SPECIFIC RESULTS: IN VIVO STUDIES

	Pathology score/Resin System			
Fabric	EA[a]	EA_1[a]	EAA	PEEK
Fiberglass	2.50(2)[b]	-	-	-
Graphite PAN/Kevlar®	1.25(3)	-	-	-
Graphite PAN		1.45(6)	2.70(4)	-
Graphite-Pitch			1.60(5)	-
Graphite-unknown				1.19(1)

[a] Polybutadiene containing resin.
[b] ( ) indicates sample number.
Note: Resin systems are EA- Epoxy/amine; EA_1- Epoxy/amine-1; EAA-Epoxy/aromatic amine.

intermediate between the two extremes with a significant increase ($p=0.05$) over aluminum oxide control noted in the quartz sample as well as two of the six composite samples (numbers 4 and 5).

Both samples exhibiting significant increases in cytotoxicity were of the same resin component which suggests that the resin portion rather than the fiber composition is responsible for increased cytotoxicity of some composite samples. However, it is noted that sample 5 is the only sample of pitch-derived graphite fiber, and this may have influenced the increased cytotoxicity of that material rather than the resin. Neither butadiene acrylonitrile composition of the materials nor the graphite PAN precursor fiber composition appeared to influence cytotoxicity (Table 5). Comparison of the in vitro with in vivo data indicates that the suggested component-related effects are not similar in the two tests.

The various mechanisms involved with the process of cytotoxicity are not completely understood. One of these mechanisms is the phagocytosis of particles by macrophage and events which follow leading to elimination of the material. Therefore, it is important to know how many dead cells have phagocytized particles. Future studies might be focused more directly on this phagocytic activity and the residence time of the particles in lung.

These in vitro data suggest a cytotoxic reaction of the composite materials with alveolar macrophages which would lead us to speculate that the initial stages of fibrotic changes in lung tissue are possible with some of the composite material dust. The extent that this process is reversible is unknown.

In vivo studies involved intratracheal injections of test chemicals into rats and pathologic evaluation of the response exhibited in the lung when animals were sacrificed 30 days later. Pathology ranking ranging between that of 0 for saline and 3.7 for α-quartz were used as an indicator of relative extent lung tissue insult. It was found that the pathological score of test samples fell within these two extremes (Fig. 1). The test materials produced a mild to moderate response (1.19-2.70) when compared to the aluminum oxide (inert dust) score of 1.10 and fibrogenic-quartz positive control of 3.70.

Overall, the pathogenic characteristic of the composite materials was that small fibrogenic lesions were common to the materials. In addition, these tissues showed inflammatory cell response, as did the aluminum oxide-treated control lungs. In contrast, the quartz-exposed lungs showed alveolar proteinosis, alveolar foamy cells, and alveolar granuloma-like lesions.

Since the 0 to 4 rating is not a linear relationship in terms of the degree of tissue damage, no statistical testing could be performed in comparing pathological ratings of control vs treatments. Therefore, it is difficult to provide an extensive interpretation of the information. The degree of damage caused by the quartz is considered much more severe than that produced by the sample materials even though the ratings using a linear scale do not reflect this.

When we consider that some of the test systems had either the same fabric cloth or the same resin system, these similarities might be reflected in the results (Table 6). Samples 4 and 5 were of the same curing agent but different graphite cloth type and exhibited different responses suggesting that the fabric is the source of the difference. If this hypothesis was correct, however, we would expect that samples 4 and 6 would elicit similar responses since the fabric in both is identical. Samples 2 and 3 had the same resin system but different cloth type, sample 2 was fiberglass and sample 3 was graphite-PAN/Kevlar®. It is suggested that the increased pathological response might be due to the fiberglass cloth, but this does not correspond with the results of the in vitro data.

Likewise, one might implicate the polybutadiene component of samples 2, 3, and 4 as causative, however, this is not confirmed since all three polybutadiene-containing materials produced responses considered intermediate between the extremes of pathologic insult.

When we compare the findings of the in vitro with in vivo results, sample 4 appears to be unique in that it ranks high in both tests (Fig. 1, Tables 5 and 6). This material is graphite-PAN and the same resin system as sample 5. Neither the same resin system nor the same graphite precursor are of high toxicity in other materials, further indicative that composition may not be the major factor in toxic potential of the composite materials. The sample materials were originally chosen partly because of the similar components in certain pairs or subgroups. However, the similarity in materials did not appear to be a factor in pathologic ranking.

Based on the findings of the morphological and chemical studies indicating the material as particulate rather than fibrous and all samples showing high chemical stability (high level of cure), it is more likely that size and shape of the particles would impact the degree of insult than would the initial epoxy chemical composition or fabric composition. Although dramatic differences in size were not discovered among the samples in the morphological investigations, there may be some subtle alterations in particle shape caused

by the method of particle production which may be responsible for the pathological differences noted. As mentioned above, the sample particles are quite durable and as such would be expected to be resistant to chemical dissolution in the lung.

In the past, data from animal studies of inhalation of carbon fiber source material (no epoxy component present) have been used as an indicator of potential hazard (Holt, 1981; Owen et al., 1986). In those studies significant lung tissue damage was not indicated. The morphological dissimilarity between raw graphite fiber and epoxy-graphite composite particulate material has been demonstrated and it is thought that it is the basis for the lack of lung response produced by raw fiber (Mazumder, 1982; Holt and Horne, 1978; Holt, 1981).

The information presented in the in vivo study presents a picture similar to the in vitro results in that both indicated the sample materials as producing a mild to moderate insult in rat lung tissue. Whether or not the lesions noted in vivo are reversible over longer time periods is not known. Likewise, the role of phagocytosis, as well as the possible dose dependant nature of the insult, are yet to be studied.

Extrapolation of Results to Recommendations for Threshold Limit Values

One method of determination of employee risk from exposure to composite materials is to compare the applicable range in airborne standards for the positive control (quartz) and nuisance dust and extrapolate the results of the toxicology study to those standards (Table 7). The current TLV (ACGIH, 1988) for quartz is 0.1 mg/m^3 respirable fraction, but the response noted in the composite dust was not as extensive as that indicated in quartz. It would appear that the appropriate threshold dust level for composite dust falls between the two extremes ranging from 0.1 mg/m^3 respirable (Quartz) and 10 mg/m^3 total (nuisance dust) although two different fractions of dust are involved in this comparison. Two approaches can be used. The first is to compare the hazard of the dust to quartz, and the result would be a threshold within the range of 0.1-5.0 mg/m^3 respirable (range between quartz and nuisance dust). The other would be to assume a somewhat constant fraction of respirable to total dust and consider a threshold for total composite dust below that of nuisance dust.

TABLE 7

COMPARISON OF DUST TYPES ACCORDING TO THRESHOLD LIMIT VALUES

Dust Type	TLV[a] or other
Fibrous Glass Dust	10 mg/m^3, Total dust
Quartz dust	0.1 mg/m^3, Respirable dust
Coal dust	2 mg/m^3, Respirable dust
Graphite, natural	2.5 mg/m^3, Respirable dust
Graphite, synthetic	10 mg/m^3, Total dust
Nuisance particulates	10 mg/m^3, Total dust
Dust, thermosetting resin	3 mg/m^3, Total dust[b]

[a] Threshold Limit Values and Biological Exposure Indices for 1988-1989, ACGIH (ACGIH, 1988)
[b] Swedish Standard with notation "dust with or without fiberglass from set or non-set plastic material" (Cook, 1987).

Sweden is the only country that we know of which has established a standard for composite dust. This value is 3 mg/m^3 total dust, and it is listed as "Dust, thermosetting resin" with a notation that "the standard refers to dust with or without fiberglass from set or non-set plastic material...." (Cook, 1987).

The composite dust is likely to be more closely related to the epoxy dust than to natural graphite or fibrous glass, morphologically, and we would consider the lower mg/m^3 range consistent with the 3.0 mg/m^3 Swedish standard to be more indicative of a composite TLV based on the data derived from the composite dust study. However, the relatively wide variability in response among the composite dust samples may complicate efforts to suggest a single dust level as predictive of a threshold.

Monitoring Data

Experience with air monitoring of composite dust exposures indicates that many operations are of short duration and intermittent, therefore, TLV comparisons do not always reflect the actual concentration of dust during the period of measurement. For work operations performed for limited time periods, oftentimes an excursion value (a multiple of the TLV or permissible exposure level (PEL)) is more applicable than the eight-hour time-weighted average as an exposure criteria.

A listing of measured total and respirable average air concentrations (time weighted over the sampling periods of varying duration) of graphite composite dust for the major production operations involving cured composite dust is presented in Table 8. The respirable and total measurements are not necessarily taken at the same time. It is noted that the total dust concentrations are quite variable even within each specific type of operation, but the lower dust concentrations appear to reside in the drilling operations and the upper range in composite cutting with grinding/sanding and routing/milling falling between those two boundaries. Drilling is usually done on a relatively small scale, and the surface area affected is smaller and drilling intermittent, therefore, the levels are expected to be lower. Cutting operations may involve larger surface areas and rather large cutting surfaces, and therefore, the dust levels may be higher. In the case of respirable dust, the highest concentrations were found within routing/milling and the lowest in grinding/sanding. This is difficult to interpret without further investigation of the specific type of equipment used.

In almost all cases, local ventilation was operable while sampling was performed. However, much of the data represents monitoring performed to determine the before vs after effects of alterations in local exhaust to provide more efficient removal of particulate materials. Therefore, these data are more likely to reflect worst case conditions than general levels of composite dust encountered at the work operations. Also, where the eight- hour TWA values were calculated for these measurements, the range of concentrations was lowered significantly. Therefore, the control of exposures to TWA levels in the range of 1 to 5 mg/m^3 can be easily attained by properly designed local exhaust in most production composite machining work. Probably the most effective local exhaust is that which is engineered into the tool.

TABLE 8

MONITORING SUMMARY FOR GRAPHITE-EPOXY DUST IN SELECTED PRODUCTION OPERATIONS (1977-1988)

Operation	n	Conc., Total[a]	Conc., Respirable[a]
Cutting	3	7.2 (7.8)	---
	2	---	4.1 (3.2)
Grinding/	5	4.3 (4.1)	---
Sanding	4	---	1.0 (0.2)
Drilling	4	0.9 (0.4)	---
Routing/	12	3.9 (4.5)	---
Milling	4	---	6.5 (6.7)
Mixed	8	4.5 (6.0)	---
Total	32/10	4.1 (4.8)	3.8 (4.8)

[a] Mean (S.D.); units are mg/m^3.
Note: These are average concentrations over sampling periods of varying duration, not eight-hour time-weighted average (TWA) values.

SUMMARY AND RECOMMENDATIONS

Several areas of exposure evaluation of composite materials processing were explored. Specific attention was focused on characterizing the morphology/chemical and toxicological properties of composite dust. The following summary of results is presented with recommendations:

1) Consideration of composite product form (cured vs uncured), type of work operation, potential routes of exposure, monitoring methodologies, relative absorption rates of chemicals, and product component toxicity are all important in assessing and defining exposure to composite materials.

2) Results of studies performed on composite dust provided were summarized and toxicology data reviewed with respect to product components.

3) Based on analysis of bulk and size fractionated samples, composite dust is particulate in nature with few fibers. Industrial Hygiene measurements on dust exposure should be based on gravimetric analysis rather than fiber counting.

4) The dust is thermally stable up to 250° C and exhibits a high degree of cure, indicating that exposure to significant amounts of decomposition products during processing is unlikely.

5) Results of toxicological studies of cured composite dust suggest that the material produces a relatively wide variation in response across different types of dust without evidence that the response is related to the presence of specific type of resin or fabric. Potency of this material to produce lung insult is greater than nuisance dust but far below that of quartz.

6) Based on toxicology findings, consideration of a TLV for composite dust below 10 mg/m^3 is recommended. Effective control of dust exposures to below the range of 1-5 mg/m^3 by local ventilation is feasible.

7) Additional research is required in the following areas:

   a) General toxicology research focused on potential exposure to composite components during processing of the materials. Additional emphasis on defining various methods to be utilized to define exposure including biological monitoring and application of various skin absorption rate determinants.

   b) Further elucidate the relationship, if any, between the lung effects/cytotoxicity of composite dust and composite chemistry as well as dose. Through inhalation studies, characterize the mechanism of the response and duration. Study more extensively the role of phagocytosis of composite dust materials as it relates to macrophage viability.

   c) Further evaluate the work environment to establish the relationship between total and respirable dust loadings for various composite processing operations.

   d) Continue investigations which would target those work processes which need special attention relative to dust control. Develop local exhaust systems which are engineered into the tool, resulting in the most effective removal of dust.

ACKNOWLEDGEMENTS

The University of Washington (UW) interdisciplinary composite research team of Drs. David Kalman, Tom Martin, Dan Luchtel, and Gil Omenn of the UW group are gratefully acknowledged for their research efforts. The Boeing Corporate Safety and Health research committee of Mike Stewart, Dr. Barry Dunphy, and Nick Novak are thanked for their ongoing assistance and direction in the graphite project. Tom O'Keeffe of Boeing, Corporate

Industrial Hygiene assisted with sample collection as well as various tasks essential to the management of the research project.

The graphite dust research project was supported by Corporate Safety and Health, The Boeing Company.

REFERENCES

ACGIH, Threshold Limit Values and Biological Indices for 1988-1989, Cincinnati, Ohio

Bartek, M.J., LaBudde, J.A., and Maibach, H.I. (1983). Skin permeability in vivo: Comparison in the rat, rabbit, pig, and man. J. Invest. Dermatol. 58:114-123.

Boatman, E.S., Covert, D., Kalman, D., Luchtel, D., and Omenn, G.S. (1988) Physical, morphological, and chemical studies of dusts derived from the machining of composite-epoxy materials. Environ. Res. 45:242-255.

Bourcier, D.R., Gokhale, R.D., Mitra, A.K., and Morris, S.L. (1986). Model for evaluation of the dermal hazard of chemicals. In, Trace Sub. Environ. Health XX, (D.D. Hemphill, ed.), pp. 165-172, University of Missouri, Columbia.

Bronaugh, R.L., and H.I. Maibach (1985). In-vitro models for human percutaneous absorption. In: Models in Dermatology, H.I. Maibach and N.J. Lowe, eds., Basel Karger, 2:178-188.

Cook, W.A. (1987). Occupational Exposure Limits-Worldwide, p. 239, AIHA, Akron, Ohio.

Holt, P.F. and Horne, M. (1978). Dust from carbon fiber. Environ. Res. 17: 276-283.

Holt, P.F. (1981). Submicron carbon dust in the guinea pig lung. Environ. Res. 28: 434-442.

Kowalska, M. (1982). Carbon fibre reinforced epoxy prepregs and composites-health risks aspects. SAMPE Quarterly, January, pp 13-19.

Lauwerys, R.R. (1983). Industrial Chemical Exposure: Guidelines for Biological Monitoring, pp. 1-7, Biomedical Publications, Davis, CA.

Luchtel, D., Martin, T.R., and Boatman, E.S. (1989). Response of the rat lung to respirable fractions of composite fiber-epoxy dusts. Environ. Res. (in press).

Martin, T.R., Meyer, S.W., and Luchtel, D.R. (1989). An evaluation of the toxicity of carbon fiber composites for lungs in vitro and in vivo. Environ. Res. (in press).

Mazumder, M.K., Chang, R.J., and Bond, R.L. (1982) Aerodynamic and morphological properties of carbon-fiber aerosols. Aerosol Sci. and Tech. 1: 427-440.

Owen, P.E., Glaiser, J.R., Ballantyne, B., and Clarry, J. (1986). Subchronic inhalation toxicology of carbon fibers. J. Occup. Med. 28: 373-376.

THE DEVELOPMENT OF WORKPLACE EXPOSURE LIMITS FOR TOXIC SUBSTANCES

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ABSTRACT

In developing a recommended TLV, ideally one should have complete data in the following areas: 1) the identity of the material which is thought to be the cause of an adverse health effect, including contaminants and decomposition products; 2) the jobs of the exposed workers, the processes they use and demographic characteristics such as age, length of exposed employment and smoking history; 3) quantitative personal exposure measurements; and 4) the health outcome being studied and its time relationships with the presumed harmful exposure. In practice, such complete data is rarely obtained but where it is, an appropriate exposure limit is frequently clearly apparent without the use of complex mathematical risk modeling procedures. Where significant gaps in the data exist, inconsistencies between different studies are difficult or impossible to reconcile and any recommended exposure limits are of dubious validity even where sophisticated observational methods or data analyses are used. Examples in each of the above categories will be described.

INTRODUCTION

In any work operation involving toxic substances there will always be some worker exposure. For substances that do not cause cancer, it is usually accepted that there is some degree of exposure below which no adverse health effects will occur in populations of normal healthy adults. This is called the threshold level or Threshold Limit Value (TLV) and it is recommended that airborne concentrations (exposures) be kept below it The American Conference of Governmental Industrial Hygienists (ACGIH), through its Committee on Threshold Limit Values for chemical substances has been recommending TLVs for toxic substances in workroom air since the early 1940s. The ACGIH is a private professional

organization whose members are occupational health professionals employed by federal, state, local and foreign government agencies (including the armed forces) and universities.

In 1970 the newly formed Occupational Safety and Health Administration adopted the 1969 TLV list of 400 substances and made them legally binding regulations. Over the next 19 years, the agency promulgated new permissible exposure levels (PELs) for about 25 substances including lead, asbestos, benzene and formaldehyde. Although 200 of the 1969 TLVs were changed (mostly downward) and 200 new substances were added, OSHA did not adopt these new values until January 1989. Currently occupational exposure limits are being developed by the ACGIH, OSHA, NIOSH, producers and users of toxic substances and by foreign governmental and nongovernmental entities. Regardless of who proposes a limit, the process of its development is the same.

DISCUSSION

The establishment of a TLV is essentially an exercise in dose-response relationships In principle, one observes the incidence of adverse health effects in people or animals at different exposure levels and then determines the level at which no adverse health effects occur; or where some effect is observed but at a rate that is somehow considered to be "acceptable". Although this appears to be a very rational approach, every word used in the above sentence is loaded with ambiguity and uncertainty. Only by assuring an understanding of every term, is it possible to assure that a recommended exposure limit will be accepted by all affected parties.

Some critical elements for determining a TLV which are frequently overlooked are: the identity of the presumably toxic substance; the levels at which people or animals have been exposed, sometimes over very long spans; the identification of the adverse health effect being prevented; and the amount of deviation from normal functioning which will be considered "acceptable" by the most relevant people, the workers.

Identification of the Material Under Consideration

It is surprising to find out how often the material suspected of causing adverse health effects is not actually the etiologic agent. In toxicological research the test agent is carefully defined and its purity carefully controlled. In the workplace, exposures are to mixtures and

frequently the nature of the materials is not well defined. The situation with amorphous silica illustrates this issue quite well.

Silica is the common name for silicon dioxide, a pure chemical compound that occurs widely in the earth's crust and in several synthetic forms. In nature, the most common form of silica is the crystalline substance, quartz, in which atoms of silicon and oxygen occur in a regular three dimensional array. This submicroscopic order is reflected in the external shape of quartz crystals which have flat faces and sharp edges. Small particles of quartz frequently have lost their crystalline appearance through abrasion but the diffraction of x-rays by the particles demonstrates their underlying internal order. Two other crystalline forms of silica cristobalite and trydimite occur naturally but are far less common. They are both pure silicon dioxide but the geometrical arrangements of the atoms are different from quartz. All three forms cause scarring of lung tissue (fibrosis) but cristobalite and tridymite are more potent.

There are several forms of pure silica in which the atoms are arranged randomly. These are called amorphous. Particles do not have flat faces and sharp edges and do not display x-ray diffraction effects. Diatomaceous earth is a natural form of amorphous silica; there are several forms which are prepared synthetically.

Diatomaceous earth is the amorphous silica which has been studied most thoroughly. Persons who process the natural material do not develop pulmonary fibrosis and it has become the accepted view that diatomaceous earth and all other forms of amorphous silica are harmless nuisance dust. Confusion arose when several studies with other forms of amorphous silica demonstrated pulmonary fibrosis in exposed workers. The differences were so striking that it seemed as if totally different substances were being studied. This was in fact the case.

Tripoli, a polishing agent, consists of very fine noncrystalline particles. But it causes fibrosis and x-ray diffraction shows that it is actually crystalline quartz. Silica gel and precipitated silica are prepared by aqueous chemical reactions while fumed silica is produced by a gas phase reaction. All three are truly amorphous and cause no known adverse health effects. But a silica fume formed in some high temperature metallurgical processes causes a short-lived pneumoconiosis even though the product is truly amorphous and shows no x-ray diffraction pattern.

All forms of amorphous silica had been assigned the same TLV, 10 mg/m^3, which is the value assigned to nuisance dust. It is clear that this is an error caused by misidentification of the toxic material. There isn't one amorphous silica, there are several with different toxicities; and indeed one supposedly amorphous silica, tripoli, is actually crystalline.

Dose and Exposure Measurements

In ordinary toxicological research, doses are carefully predetermined and administered in accurately measured amounts. In the workplace, the most common route of entry for toxic substances is by inhalation, and in animal experiments used to estimate the potential for adverse health effects in humans, toxicants are administered by inhalation. In these cases, dose is not measured directly; it is calculated from a measured airborne concentration and an assumed breathing rate.

In animal experiments, the actual delivered dose can be quite variable, which causes a corresponding variability in the incidence of disease. Many airborne toxicants cause alteration of breathing rate and this creates uncertainty in the quantity of material actually taken up by the animals. Also many animals preen their fur and accordingly ingest dust deposited on it. These and several other effects make it difficult to compare effects from different routes of administration and to extrapolate from animal experiments to human experience.

In studying the effects of toxic substances in humans, experimental exposures are becoming less and less common. Most commonly, the health status of persons who are exposed to hazardous materials in their normal work situations is determined. Doses, of course, cannot be determined; rather airborne exposure levels are measured and it is assumed that they are proportional to inhaled doses. This assumption is only approximately correct. People vary in their breathing rates depending on body size, race and gender; and the fraction of an inhaled dose deposited in the lungs depends on breathing rate, particle size, solubility and mouth vs nose breathing. This means that the dose received by different groups of workers may not be completely characterized by their airborne exposures.

The major cause of inaccuracy in characterizing exposure, and thus dose, is the sparsity of exposure measurements and the inappropriateness of the measurement protocol. In most cases airborne exposures have not been measured with a view towards supporting the development of an occupational exposure limit. Measurements are frequently taken to

assess compliance with existing standards, to localize or determine exposures associated with employee complaints, to evaluate the effectiveness of ventilation systems and, in some cases, to evaluate the validity of compensation claims. Measuring exposures in a systematic way can be expensive and unless employers can see benefits for themselves, they will not do it. Because of the shortage of good exposure measurements the TLV Committee uses whatever data is available and then to accommodate inaccuracies, a safety factor is applied. If one is in the enviable position of being able to plan a monitoring campaign prospectively, it is possible to develop data which will be of maximum use for establishing valid occupational exposure limits.

It has been accepted for several years that the time spans over which airborne exposures are measured should be similar to the biological time periods over which adverse health effects develop. Thus for primary irritants which act almost instantaneously, very short sampling times or direct reading instruments are needed. (Incidentally, health effects may also have to be observed in "real time", for instance by observing or asking about subjective effects.) Where a health effect is the result of the cumulative dose during a single work shift, then eight-hour time-weighted averages are recommended. Where an effect is the result of a very long exposure, such as lung fibrosis or cancer, then complex statistical methods are needed to calculate a "life-time" cumulative exposure from a set of exposure measurements taken over a long period of time. Exposures in the past are frequently estimated using records of production volumes and the installation of ventilation or by interviewing workers and management staff.

Identifying the Adverse Effects

In the development of an occupational exposure limit, it goes without saying that the health effect being controlled is identified. Not infrequently there are disagreements as to whether an observed alteration in biological function is a symptom of illness, is within the range of normal function or is merely a nuisance. Where an effect under consideration is life shortening or is universally recognized as an illness requiring medical treatment, there is no argument. However it should be recognized that the goal of occupational health (and all of public health practice) is the maintenance of good health and not just the prevention of illness and lost work time. Thus TLVs are established to prevent transient ill effects such as headache and irritation even where these do not result in permanent injury, the shortening of

life or some kind of medical treatment. Transient ill effects constitute a degradation of good health and, in an economic sense, they decrease productivity when workers spend time complaining to one another and to their supervisors or visiting plant health facilities; or filing compensation claims or labor/management grievances.

In another dimension, some workplace exposures cause deviations from normal body functioning without creating an effect that a worker would notice as an ill effect. For instance, exposure to soluble cadmium compounds above certain levels can cause a serial decline in kidney function. Small decrements can be accommodated by the adaptive capacity of the body; but the changes are permanent and if exposures continue, a definite disease state may result, perhaps only after retirement. Thus a TLV will be set at a level which results in no decline in body function at all or one which is similar to what occurs as a result of normal aging.

Deviations From Normal Functioning

In the normal functioning of the human body, physiological parameters can take on a continuum of values with no natural distinction between "normal" and "abnormal". Rather, there is a range of values observed in apparently healthy people (with no reported symptoms) which is declared to be normal. Values outside this range are called abnormal but it is not always clear whether such abnormal values constitute "disease" per se or are precursors of overt illness at some time in the future. For instance, persons unexposed to lead except through water and food have blood lead concentrations in the range of 5-15 μg/dl. People who work with lead frequently have blood lead levels in the 20s without displaying any recognizable symptoms and apparently not suffering any ill effects even after many years.

To some extent, the boundary between normal and abnormal function is arbitrary. Where a physiological parameter such as pulmonary function or liver function has been measured, normal and abnormal are frequently differentiated on the basis of the statistical distribution of observed values. For instance, abnormal functional values are sometimes defined as those that occur above the 95th percentile. This creates the situation where 5 percent of the population is defined as "sick" or "abnormal" when there may be no other evidence of illness. On the other hand, the group on which most functional parameters is measured is not representative of the normal healthy adult population. They were tested

when they consulted a physician because of perceived illness. It would not be surprising to find that their tests differ from a truly normal population.

Occupational exposure limits are chosen to prevent the development of illness. Where the function affected by a workplace contaminant occurs on a continuum it is necessary to define the boundary between health and disease and to specify an exposure limit which will prevent disease. When this is not done in a conscious manner, different people will set different boundaries and will recommend different exposure limits. Sometimes this lack of specificity is not easily recognized and conflicts between different recommendations are resolved by political means rather than scientific ones or perhaps not at all.

CONCLUSION

One of the aims of toxicological and epidemiological research on industrial chemicals is to determine a recommended (presumably safe) exposure level (e.g., TLV) below which illness, in the broadest sense, will not occur. Whether the level is derived from sophisticated mathematical risk modelling, animal experimentation or just professional judgement, the four kinds of information discussed in this paper must not be overlooked.

- The identities of the substances in the work environment must be clearly recognized. Where animal experiments are used to evaluate toxicity it is important to assure that the test compound is actually the same as the one in the workplace. Solubility, crystalline form and particle size are significant variables. In the workplace, toxic impurities can confound otherwise valid conclusions.

- The airborne concentrations to which workers are exposed are a critical factor and are difficult to determine. Special efforts must be made to evaluate worker exposures, sometimes over very long time spans. In the development of Threshold Limit Values, exposure estimates are frequently inadequate or entirely missing.

- The adverse health effects which are to be avoided must be identified and should be ones that are significant from the workers' point of view. Consideration should not be restricted only to those effects traditionally considered to be forms of ill health.

- The philosophical question of what constitutes a significant deviation from normal health should be faced squarely.

V. ENGINEERING CONTROLS AND WORK PRACTICES

CONSENSUS STATEMENT

The purpose of engineering controls and work practices is to control exposures to prevent adverse effects. For the purposes of this analysis, exposures can be categorized as occurring either in the manufacturing and production industries, or as the result of maintenance and repair functions. These latter can be further subdivided into depot-level, intermediate-level, and field operations.

Based on many years of operational experience, the knowledge exists to properly design both facilities and equipment to either isolate or contain toxic materials, or to minimize exposures to them. When properly maintained and used as designed, these facilities and equipment do indeed adequately control exposures since adverse effects are infrequently reported.

At the depot level, conditions are generally similar to but on a smaller scale than those in the manufacturing and production facilities. The conclusions drawn above apply. At the intermediate and field levels, however, it is unclear to what extent engineering controls can be used and with what degree of success.

NEEDS AND CONCERNS

New technology (automated materials handling, robotics) for containing or isolating many operations offers the potential for eliminating many exposures; however, this is also very expensive technology. Initiatives to reduce the cost of such equipment are needed.

Much innovative work has been done to control exposures using engineering controls in the complex and idiosyncratic operating environments of the composites' manufacturing and production industries. Most of this work is not generally known outside the company which sponsored and uses it, yet it may well have wider applicability. The ACGIH Industrial Ventilation Manual or other widely recognized resource should be used to disseminate this information.

Two forms of periodic monitoring are required to ensure engineering controls are and remain adequate. The first is industrial hygiene monitoring of exposure levels to ensure the equipment is performing as intended. Exposure levels found by such monitoring should be

considered in a manner similar to the ventilation designs mentioned in the previous paragraph, and treated analogously. The second is medical monitoring of exposed personnel to ensure that their exposure is not causing any adverse effects. This topic is dealt with elsewhere in more detail.

WORK PRACTICES

Requirements for work practices necessary to supplement engineering controls, or to substitute for engineering controls when those are not practical, have been identified and implemented. Experience has validated their efficacy when implemented as an integrated program based on job hazard analysis, and when used properly and conscientiously. Included are personal protective equipment, housekeeping, employee feedback opportunities, labeling, and process specifications (not an exhaustive list). An integral part of a successful work practices program is thorough employee training and routine hazard communication, addressed elsewhere in this document in more detail.

While the same work practices remain valid in general, their ability to replace engineering controls in providing adequate exposure control when those are not available remains in doubt. This is likely to be a significant problem at the intermediate and field maintenance levels. The depot-level should function sufficiently similarly to manufacturing and production facilities that the same solutions will be equally applicable.

Personal protective equipment, while generally adequate, is not always satisfactory. Gloves are a good example of the nature of the problem. Many manufacturers make protective gloves of various materials to resist penetration by different chemicals. Review of their literature reveals significant variability in their claims for resistance -- for what is supposedly the same material. No standardization exists, or even guidelines for standardized testing. It is proposed that the composites' industry develop a set of requirements or specifications for protective gloves, and an estimate of the potential market for such gloves, and approach the glove manufacturers to determine whether this would warrant their making available such a glove.

A related factor is the difficulty in selecting the appropriate work practices (e.g., personal protective equipment, training) for a given material in a specific operational environment. This is complicated by the frequently inadequate information provided on many

MSDSs. While this is dealt with in detail elsewhere, its impact on this topic bears repeating here.

The need for periodic monitoring of the effectiveness of engineering controls described earlier is also relevant for ensuring the effectiveness of work practices. Further, data regarding work practice effectiveness should be treated similarly.

EMERGENCY PREPAREDNESS

Emergency situations are created when (1) the failure of equipment or work practices results in the sudden, unexpected release of toxic material into the work area, or (2) a runaway exothermic reaction, fire, and/or crash releases thermal decomposition products and fibers into the environment. Procedures to control such events, and the attendant personnel exposures, have been implemented to varying degrees throughout both the manufacturing and production industries and in maintenance and repair activities. These include written SOPs, appropriate training, periodic drilling, and ready availability of emergency response equipment (including frequent inspection and maintenance).

Emergency situations involve the potential for exposure to a complex mixture of materials whose composition, concentration, and toxicity (either singly or as part of a mixture) are not clearly defined. In the absence of such data, the highest degree of protection (e.g., use of SCBA vice negative pressure respirators) is required. The causes of such events must be identified and minimized. Appropriateness of procedures and protective measures must be evaluated by hazard analysis, with periodic review as new toxicological data becomes available.

ENGINEERING AND WORK PRACTICE CONTROLS FOR WORKING WITH ADVANCED COMPOSITES: MINIMIZE WORKPLACE EXPOSURES

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ABSTRACT

Neither engineering nor work practice controls should be looked upon as an exclusive remedy to exposures created by advanced composites in the workplace. Each should, however, be viewed as working in concert with the other to minimize attendant exposures and their potential.

Materials utilized in Hexcel operations create exposures in the form of dust, fibers, liquids, vapors, mists, decomposition, and combustion products. Hexcel's primary focus for controlling exposures is through two basic engineering approaches: isolating or containing materials and providing ventilation. Isolation is applied for both storage and process usage of certain materials. Providing enclosures or closed systems to contain certain segments of operations is also used.

Ventilation is also utilized with the primary focus being on local exhaust. Provisions for make-up air are important to the proper functioning of all exhaust ventilation systems.

Work practices, if properly implemented, can be as or more effective than engineering controls in reducing workplace exposures. Hexcel incorporates six elements into the area of work practices: job hazard analysis, protective equipment, good hygiene practices, housekeeping, hazard communication, and emergency preparedness.

Feedback mechanisms are important to maintaining effective engineering and work practice controls. Hexcel utilizes five: periodic ventilation checks, exposure monitoring, medical surveillance, job observation by supervision and employee comments.

PRESENTATION

Good morning, I appreciate the opportunity to address this conference and share with you information regarding Hexcel Corporation's forty years of experience working safely with advanced composites in our operations.

Engineering and work practice controls have been and continue to be major components in Hexcel's occupational health effort. Neither of these important areas should be looked upon as an exclusive remedy to exposures created by advanced composites in the workplace, but each should, however, be viewed as working in concert with the other to minimize attendant exposures and their potential.

The materials utilized in our operations create exposures in the form of dust and fibers, liquids, vapors, and mists and decomposition and combustion products. Routes of entry that we must control are inhalation, skin contact, and ingestion (low percentage). Looking at where the potential for these exposures exists in our operations:

Dust and fibers are encountered when processing or handling fiberglass, graphite, ceramic, quartz, and aramid fiber materials. Examples would be at impregnation towers and tape lines. This problem is also encountered during the machining of materials which include slitting, sawing, milling, and various hand tool operations such as routing, grinding, and sanding. Potential dust exposures must also be controlled in resin mixing areas where powdered materials are weighed and added.

The potential for contact with liquids and exposure to vapors is presented in our mixing areas, at impregnating towers, tape lines, curing presses, and when handling "B" stage material. In our honeycomb operations, when flow coating, dipping and curing blocks, and when working with adhesives and core-fill materials. The potential for decomposition and combustion products is encountered whenever uncontrolled exothermic reactions take place. This can occur when mixing or handling catalyzed resin systems and in curing ovens. These events are unplanned and are treated within Hexcel as emergency situations.

Hexcel's primary focus for controlling workplace exposures is through the application of engineering controls. Two basic approaches that have been taken to accomplish this: isolating or containing materials and providing ventilation.

Application of the first approach consists of providing isolated storage or separate process areas, such as resin mixing and honeycomb block dipping; providing enclosures to contain the exposure generating areas of impregnating towers and incorporating closed systems where possible, such as in the mixing and transfer of resin solutions.

The second basic approach to engineering controls is through the use of ventilation. Our primary focus is on local exhaust ventilation as it is the most effective in removing airborne contaminants from the workplace and reduces the need for replacing temperature

and humidity controlled air in winter and summer months. General or dilution ventilation is also used to provide from three to five changes of air per hour in the work area. This helps to reduce buildup of contaminants that may not be captured by local systems. Provision for make-up air is important to ensure the proper functioning of both local and general ventilation systems. We have used make-up air in tandem with local exhaust systems, creating a push-pull type system and enhancing the system's overall effectiveness. It is important to closely regulate the use of pedestal fans as these units can compromise local exhaust systems that are in place and cause contaminants to enter the workplace that would otherwise be exhausted. The use of recirculation systems (those which reintroduce the exhausted air back into the workplace) is very limited when dealing with exhausted contaminants. It is used only for nuisance particulate and fibers and then reviewed on a case by case basis. As an added comment on engineering controls, it is important that they are designed and installed to be compatible with current work practice and ergonomic requirements which will increase the likelihood that they will not be circumvented or rendered less effective.

Moving now to the area of work practices. As previously stated, we view work practices as complimentary to engineering controls that are in place. If properly implemented, work practices can be as or more effective than engineering controls in reducing workplace exposures. Hexcel incorporates six elements into the area of work practices.

A job hazard analysis is developed for each job that is performed. This entails a complete job review or analysis to identify and outline preventive measures for injury- and health-related exposures. The job hazard analysis when completed becomes an invaluable tool for training, safety meetings, performance observations, and incident investigations. Examples of practices addressed by the job hazard analysis process include: the use of protective equipment, how to safely handle materials, etc.

Hexcel utilizes a variety of personal protective equipment (PPE) to protect employees from exposures presented by handling and processing advanced composites. Skin protection is addressed through the use of gloves, work clothing, and disposable protective clothing. Gloves are generally made of butyl or latex rubber or PVC. Barrier creams are used in conjunction with gloves, but never as sole protection. Eye protection is provided by standard safety glasses with sideshields and goggles or a faceshield, as needed.

The type of respiratory protection used within Hexcel ranges from disposable nuisance dust respirators to self-contained breathing units. Nuisance dust respirators are utilized for areas in which advanced composites are machined. Organic vapor respirators are used in operations where solvent or curing vapors are present. Self-contained breathing units are utilized only for emergency situations such as "exotherms" or chemical spills. Respirators are not used to reduce exposures to below current TLVs but rather on a task basis to reduce intermittent exposures.

Good hygiene practices are important in reducing exposures to advanced composite materials. Skin care and wash facilities are provided which enable employees to wash exposed skin areas and to apply protective and replenishing creams to their hands. Separate lunch rooms permit employees to store and consume food and beverages away from chemical areas. Cleaning and storing of PPE is also monitored to ensure that this equipment does not become contaminated and create exposures when used. This is especially important for gloves and respirators.

Housekeeping is also important in reducing exposures to advanced composite materials. Vacuum cleaning is emphasized in favor of blow-off to eliminate airborne materials and accumulation in the work area. Contaminated surfaces can contribute to dermatitis and skin absorption for certain materials.

Hazard communication is important to ensure that employees are knowledgeable of the materials they use. We feel strongly that each employee plays a significant role in determining his/her daily exposure to hazardous materials. When informed and aware, employees are much more apt to adhere to good work practices.

Exposures to materials during process upsets or emergencies are avoided or minimized through effective preplanning. Conditions such as spills or uncontrolled or runaway exotherms create concentrations of toxic materials to which employees should not be exposed. Clearly defined responses to these situations are communicated to each employee and periodic drills conducted. Equipment such as emergency showers, eyewashes, and self-contained breathing units are also available to protect employees.

Feedback mechanisms are important in maintaining effective engineering and work practice controls when working with advanced composites. These five mechanisms are utilized within Hexcel.

Periodic checks of ventilation controls should assure that equipment is functioning to design specifications. Smoke tests will determine if desired flow patterns are being attained and gauges will provide information on when filters need to be changed.

Exposure monitoring is conducted routinely to ensure that employee exposure levels are well below current or proposed limits.

Medical surveillance is provided as a "safety net" to detect problems in their early stages.

Supervisors have a major role in this effort through their day-to-day observations. As a part of their daily routine, each supervisor should monitor compliance with prescribed work practices, check condition of protective equipment, and detect early signs of problems such as dermatitis.

The final feedback item is attentiveness to employee comments, e.g., offensive smells, discomfort from materials, or the ineffectiveness of certain protective equipment. These may seem like small problems, but supervisors should investigate such concerns to determine the reason for the problem. It is not sufficient to just protect our employee's health. We want our employees to feel that their health is being protected.

ENGINEERING CONTROLS AND WORK PRACTICES

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ABSTRACT

This presentation describes the engineering controls and work practices utilized in the Grumman composite parts manufacturing facility in Milledgeville, Georgia. Included in engineering controls are air conditioning, ventilation, down draft tables, exhaust hoods, exhaust booths, point of operation vacuum systems and autoclaves.

The work practices utilized and discussed include the wearing of personal protective equipment, and the utilization of safety releases, hazard-grams and hazard communication standard training, as well as the control of the work process by process specifications.

The presentation concludes with a discussion of the employee exposure monitoring program at this facility, along with some representative monitoring results.

INTRODUCTION

This presentation will be divided into three basic areas: engineering controls, work practices, and monitoring and results. The Grumman Milledgeville Georgia Facility is among the largest and most modern sources of high strength, lightweight components for a wide range of aerospace products and other applications. It not only produces advanced composites, metal bonded, injection and compression molded and thermoplastic parts, it provides on site design and engineering support as well.

The facility is located approximately 100 miles southeast of Atlanta and 30 miles northeast of Macon. Situated on 164 acres, the main plant occupies 390,000 sqare feet. Support buildings add over 100,000 square feet.

The Grumman work force at Milledgeville numbers 564 employees and was drawn for the most part from the surrounding region. Once hired, these employees were provided with detailed job training and a specified safety training program as required. The work force would be best characterized as productive with a relatively high level of morale and job satisfaction.

Milledgeville is currently turning out more than half a million parts annually for Grumman and other aerospace companies. (F14, Transcowl, Osprey, and other programs are supplied). Advanced composite structures are fabricated from boron, Kevlar®, graphite or fiberglass fibers impregnated with polyester, epoxy, phenolic polyimide or silicon resins. The resulting "prepregs" are cut to size, shaped under vacuum on a mold form, cured under pressure, and heated in an autoclave to harden the resin and join the plies into a solid laminate. Trimming, inspection, assembly and painting complete the process.

Proper air movement in the workplace is absolutely necessary to ensure the employee is not put at risk. The design of the facility and the attendant heating, ventilation, and air conditioning (HVAC) systems should provide effective removal of air particulates and other contaminants expected to be present in the workplace. In addition to the design of the HVAC system, its operation and maintenance will dictate the degree to which the system adequately turns over the air supply in the facility. It should be understood that worker protection at a specific work station or in a paint booth may need to be provided by personal protective equipment, such as a respirator, but we must recognize that the first level of worker safety comes from a clean, contaminant free air supply in the workplace. At Milledgeville our ventilation and air conditioning systems provide an effective first level of engineering control.

The building is equipped with 38 air handling units which supply cooled air to various departments. The composite layup rooms are cooled to a constant temperature of 68° to 70° F year-round and maintained at 60 percent relative humidity. The paint shop painting booths are provided with 96,000 cfm of warm dry air. The pretreatment line is supplied with 87,500 cfm. There are six roof-mounted exhaust fans located in this area for the removal of toxic vapors. The offices are air conditioned. All shop areas which are not air conditioned are ventilated.

We've discussed the importance of a well-designed, well-maintained ventilation and air conditioning system as the first level of engineering control. Now let's look at several more specific engineering controls which we make use of at our Milledgeville facility to enhance worker protection. These would include the following: exhaust booths, exhaust hoods, downdraft tables, point of operation (portable) vacuum systems, and autoclaves.

Exhaust booths are used when sanding or trimming of the composite part is required and the part is too large to fit on downdraft tables or in front of an exhaust hood. Air supply in the booth is recirculated through a series of dry filters which capture the fines. These filters must be monitored to insure replacement at the proper time. If the particulates captured in the filter become too concentrated, the airflow will be impaired and the air supply to the booth will not provide sufficient protection.

Exhaust hoods are used for sanding or trimming composite parts of smaller size. The air is drawn across the work surface and exhausted through a dust collector.

Downdraft tables have expanded metal tops upon which a composite part is sanded or trimmed. The fines created by working the particular part are drawn down through the perforations by a vacuum action under the table top. The dust is filtered from the air and collected prior to discharge of the air.

Point of operation vacuum systems are especially effective at the numerous machine tool locations where a composite part is to be worked. The vacuum system is set up to capture the fines as they come off the tool. The fines are then filtered out in the vacuum unit.

Autoclaves are engineering controls as well as process controls. Parts are bagged and put into the autoclave. The autoclave is sealed and purged and an inert gas environment is introduced into the clave, while a vacuum is introduced under the bag. The part is cured at an elevated temperature and pressure in a process isolated from the workplace.

While OSHA rates engineering controls as the preferred method of worker protection, in some instances the controls we have reviewed are just not feasible or applicable. Work practices pick up where engineering controls leave off. The employee's use of personal protective equipment, safety releases, hazard-grams, the hazard communication standard requirements and process specs greatly enhances the safety of the workplace.

At Milledgeville various types of personal protective equipment are required as part of the job function. In areas of the plant posted for high noise (> 85 dBA), hearing protection is accomplished through the use of ear plugs and in some cases the additional protection of muffs. Working with composites, a typical noise area would be the trim room.

Eye protection is promoted through the required wearing of safety glasses in the manufacturing area of the plant. Wherever welding is being done or chemical splashing might occur, job-specific eye and face protection is required to be worn.

Employees in certain processes are required to wear gloves for hand protection. Grumman employees handling solvents or epoxy resins would wear flock-lined latex gloves. Gloves are also used at Milledgeville in cutting operations and in handling graphite and adhesive application such as on the Transcowl. Full body protection is sometimes required in which case a disposable Tyvek® suit would be worn.

Barrier creams are provided to workers at certain stations to provide additional skin protection, specifically preventing skin absorption of certain chemical constituents. In addition, simple skin irritations are greatly minimized. For example, Kerodex® 71 is the only barrier cream approved for use in the layup room, though it must be applied outside the work area.

In areas where engineering controls do not adequately reduce the level of contaminants, respiratory protection must be worn. This is typically indicated by exposure monitoring which is regularly performed. Additionally, professional judgement is employed

Employees whose work operations require respiratory protection must be certified. This certification involves a medical evaluation (including a pulmonary function test); fit testing of their actual respirator in a challenge atmosphere; and instruction on the use, limitations, and maintenance of their respirator.

OSHA is chartered with the responsibility for establishing permissible exposure standards, work practices, and regulatory requirements to ensure the protection of employees and to minimize occupational hazards. A significant component of OSHA's comprehensive regulatory network is the Hazard Communication Standard. The Standard requires employers to provide workers with detailed information on all hazardous substances to which they may potentially be exposed.

In accordance with our corporate philosophy relating to occupational safety and health issues, Grumman Corporate Procedure A711 was drafted to safeguard the health of all employees while ensuring the satisfaction of all regulatory requirements. This document is endorsed by top management.

Upon assignment of an employee to a new job, or when a new or modified hazard is introduced into the workplace, all employees involved with hazardous substance are trained, not only in the related hazards of the material, but in proper procedures for avoiding accidents and minimizing hazards. Such precautions would apply both to the more obvious situations in which chemicals are transferred to more mundane activities including the final

collection of all material, fibers and dust produced during manufacturing. While proper safeguards must be utilized in working with any hazardous substances (including personal protective equipment and engineering control systems) and emergency procedures must be prepared and rehearsed, the development of appropriate handling precautions provides the first line of worker safety by minimizing the dependence on these external controls and procedures while ensuring employee protection.

Grumman Corporation's Hazardous Materials Identification System has been designed to provide proper labeling in accordance with the Hazard Communication Standard. More importantly, though, the specific configuration of our labels provides for effective and immediate employee awareness, not only to the presence of a substance of concern in the workplace but to the relative hazard posed by that substance. Labels are developed for each material following the classification of that material with regard to its health, flammability and reactivity hazard. Labels are affixed to each container in which a substance is present. Employees whose job functions may bring them into contact with these materials are fully educated on the Hazardous Materials Identification System and are immediately alerted to the relative potential risk posed.

Also shown in circles at the bottom of the label are one or more "hazard-gram" numbers. "Hazard-grams" provide important information regarding the workplace use of material.

The net effect of Grumman's labeling system is to provide each employee with straightforward information on the potential hazard posed by a regulated material. Numerical rankings allow for immediate recognition of the severity of a potential hazard while hazard-grams provide important information regarding proper material handling.

The hazard-gram is a generic device we developed to provide information in terms of personal protective equipment, start-up and shutdown checks, and general cautions to be followed. The hazard-gram is on a three by five format which easily fits in the pocket. There are currently 13 different hazard-grams.

The hazard-grams for composites, smoothers, potting compounds, and thermosets provide quick basic information. Emergency information in the event of a splash or spill and emergency phone numbers are on the flip side of the card. Hazard-grams have been in use for five years and are an effective part of our hazard communication program.

Grumman Corporation has a policy of compliance with governmental rules and regulations. To assure that this policy is complied with we have an ongoing industrial hygiene monitoring program. This program gives us the opportunity to evaluate engineering controls and prescribe personal protective equipment, both of which enable us to adequately protect our employees. The data reflect TWA ranges for organic and inorganic exposures resulting from operations at our composite facility.

We have done a lot of solvent monitoring. Quite often this is an indicator of the potential degree of exposure to other constituents in the mixtures. Toluene sampling results show very low exposures.

Our illness incidence rates for this facility are extremely low - being mostly contact dermatitis. We are satisfied that we are providing a safe and healthful workplace. We think that we have developed the safety programs appropriate for working with composite materials. Our injury/illness experience in this plant verifies this.

ENGINEERING CONTROLS AND WORK PRACTICES FOR ADVANCED COMPOSITE REPAIR

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ABSTRACT

The advanced composites flying on today's high-performance aircraft consist of high strength/stiffness fiber imbedded in polymeric matrices. Generic advanced composite repair procedures were discussed in "Introduction to Supportability of Advanced Composites." This paper will discuss the engineering controls and work practices involved in these repairs. The repair of these materials can be done safely, but does require the worker to wear personal protective equipment (PPE) during depaint, when grinding or sanding, and when using laminating resins or uncured preimpregnated composites (prepregs).

BACKGROUND

The Air Force has three aircraft now in service with original structures made from advanced composite materials: the F-15, F-16 and B-1B. Programs at various Air Logistics Centers (ALCs) have added composite structures to the C-130, C-141, A-10, F-111, and T-38. Most of the repair experience for advanced composites is with the F-15 and F-16. These are repaired at Warner-Robins ALC (WR-ALC) and Ogden ALC (OO-ALC), respectively. Sacramento ALC (SM-ALC) has a small composite panel on the F-111 that has required minor repairs. Oklahoma City ALC (OC-ALC) is just entering the composite repair business as the B-1 enters depot maintenance.

DEPAINT

There are two methods that are currently used to depaint advanced composite structures: plastic media blast (PMB) and sanding. PMB is a depot-level depaint method that uses plastic beads of a given hardness to impinge on the painted surface. PMB can be a large-scale operation when depainting an entire aircraft or can be done on single components in a glove box. It is the depaint method that will be used by all five Air Logistics Centers to replace chemical paint stripping.

When PMB is done in a glove box, it is in a closed environment and there is no need, therefore, for the operator to wear PPE. The large-scale PMB operation is another matter, however. Technical Order (T.O.) 1-1-8, Application of Organic Coatings, Aerospace Equipment, Section 2-14 gives the general procedure for large-scale PMB. This procedure is modified as necessary by the specific weapon system manager to meet the unique requirements of that system. These modifications may include different blast pressure or stand-off distance, removal of various panels, or the removal of other panels from the aircraft before the PMB procedure begins.

T.O. 1-1-8, Section 2-14 (6) gives instructions on the PPE that should be worn during PMB: Personnel involved in PMB shall wear coveralls with full-length sleeves, gloves with gauntlets, and full air-supplied respirator-type hoods and hearing protection which meet AFOSH STD 161-1 requirements. Hoods shall be put on prior to entering the blasting area and shall not be removed until after exiting the blasting area. Hoods shall be stored in a clean dust-free area and shall be cleaned to remove all dust accumulations on them prior to storage after each use. All personnel entering the blasting area while PMB is in progress, even though not involved in the operation, shall also comply with these personnel protection requirements.

Additional requirements are levied on the base bioenvironmental engineer (T.O. 1-1-8, Section 2-14 (5): The facility used for PMB shall have adequate airflow/ventilation to prevent build up of an explosive dust moisture. The base bioenvironmental engineer shall be consulted for proper ventilation requirements.

Sanding is the method of depaint that will be used for individual panels and small area repairs in both the field and the depot. Various devices can be used to do this: a rotary sanding disk, a self-addressing flap wheel, or a high velocity/low volume orbital sander. The first two require the mechanic to wear a dust mask and either use a vacuum attachment or perform the operation in a downdraft booth. The reason for this is that many of the paints found on aircraft contain lead and the primer contains chrome. Wearing the mask and removing the paint particulates limits worker exposure to these metals.
The high velocity/low volume orbital sanders used by mechanics at SM-ALC have vacuum attachments that remove paint particulates from the area without the mechanic having to hold a separate vacuum hose. This type of operation can be done on the shop floor with no special PPE or environment.

REPAIR OPERATIONS

The first step in the repair operation is removal of the damage. The level of damage will dictate the amount of material removed - the less material removed, the better. The type of repair will also dictate the size of the repair area. Only the damaged area will be cut away for a scab patch repair. For a step or scarf repair, the damaged area must be cleaned up and then the steps/scarf must be machined into the area surrounding the damage.

Damage removal and stepping/scarfing is typically accomplished with a router or a rotary disk sander. The mechanic must wear a dust mask, and a vacuum or downdraft booth must be used to collect the dust. There are precautions in the various T.O.s concerning the machining of composites. T.O. 1-1-690, General Advanced Composites Repair Manual, Section 1.9 lists several safety precautions. One of these is: damaged composite components may be hazardous to your health. Single fibers can easily penetrate the skin, break off, and become lodged beneath the skin. Graphite composite components damaged by fire may be covered with dust.

Single-fiber dust particles with a diameter of four microns and length of less than 0.004 inches pose the greatest threat to the respiratory system. Respiratory protection is necessary for those operations in which dust is present or generated. The dust should be removed through a vacuum system and properly disposed of as a hazardous material. Eye protection, consisting of safety goggles or a face shield, is also recommended for any operation where the likelihood of airborne fibers exists.

Boeing recently invented a router with an integral vacuum attachment called a Scarf-O-Matic® that machines excellent scarf angles into the laminate. They report that there is no dust generated and the machining operation may be done on the open shop floor.

The next step in the repair operation is to replace any substructure (honeycomb core, integral stiffeners, etc.) and apply the repair patch. Wet layup, procured patch, and prepreg repairs all pose a similar health risk to the mechanic. Most of the composite structures flying today consist of graphite fibers in an amine-cured epoxy resin matrices. The resins used to repair these structures, be they the laminating resin for the wet layup, the film adhesive for the procured patch, or the resin in the prepreg, will generally be amine-cured epoxies. The Material Safety Data Sheets for these resins warn of the potential of dermatitis if they come in contact with the skin. Gloves should be worn when handling these materials. Rubber gloves

are required when using the laminating resins; lint-free cotton gloves are more appropriate when using film adhesives and prepregs.

The final step in the repair process is curing the adhesive or prepreg. This is done with the application of heat and pressure. Depots will have autoclaves in which to cure their laminates. Autoclaves are not practical pieces of equipment for field units; a portable heat and vacuum unit called a "hot Bond" is used. No PPE is necessary for the curing operation other than gloves to protect the mechanic from hot tooling.

FACILITIES

The grinding operations involved in damage removal and scarfing of advanced composite structures can be very messy. The first time one of our mechanics tried it in an updraft booth used at SM-ALC for conventional fiberglass work, he came out black. The carbon dust given off had covered him from his chest to the top of his head. That was the last time graphite/epoxy was machined in that sanding booth. Since then, one small downdraft booth has been used for machining operations.

A second feature that is essential is a vacuum system to either be held by the mechanic as an open hose or hooked into the piece of grinding equipment. It should be noted that the debris picked up by the vacuum system should be treated as toxic waste. It will contain the lead and chrome from the paints, asbestos from old adhesives, carbon dust, etc.

The autoclave is a piece of equipment with hidden dangers. Both the vessel and the vacuum lines from the individual parts should be vented outside the building. One autoclave at SM-ALC was not vented outside the building until recently because of a piping mix-up. The base bioenvironmental engineers took air samples and found that the volatiles coming off during normal epoxy cures presented no hazard to personnel in the area. This overlooks what the consequences would have been had there been a fire in the autoclave. There would have been nowhere to vent all the noxious and potentially toxic fumes except out into the plant. A second concern arises when curing condensation resins such as phenolics. The volatilized chemicals arising from curing resins are generally water, methyl alcohol, or ethyl alcohols. Solvents and low molecular weight monomers such as xylene, trimethyl foramide, n-methyl pyrrolidone, formaldehyde, and phenol.

CLOSING

Advanced composites have been on Air Force aircraft for more than 15 years. Until recently there have been no reported major health problems associated with advanced composites. Plants where composite structures are fabricated and repaired can be made safe if plans are made for the proper facilities and a little common sense is used. The Air Force must keep these considerations in mind as it prepares to meet the expanding advanced composite repair work load it will face in the future.

INDUSTRIAL VENTILATION SYSTEMS

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ABSTRACT

An industrial ventilation system simultaneously supplies air to and exhausts air from a workplace to control contaminants. The major goal of the mechanical system is to maintain a negative pressure in the room to prevent contaminant migration from the controlled area. The Naval Energy and Environmental Support Activity (NEESA), Occupational Safety and Health Group strives to improve Navy industrial ventilation systems in three major areas: design review, system performance/acceptance tests and system design training.

This presentation discusses the basics of system design including: replacement air distribution, balanced vs blast gate methods for exhaust systems, enclosed vs standard hoods, duct transitions and entries, fans, air pollution control devices and stacks. Our experience includes fiber reinforced plastics (FRP) operations. FRP operations present ventilation problems similar to composite operations since both dust and solvents are produced during fabrication and repair.

System acceptance/performance testing is a critical but often neglected part of a construction contract. The tests must be complete and the data turned over to responsible parties in both the public works, and health and safety departments. These people are responsible for annual (or more frequent) system performance tests.

The final aspect of NEESA's program is training both mechanical designers and industrial hygienists to properly design and review industrial ventilation systems.

INDUSTRIAL VENTILATION SYSTEMS

Industrial ventilation systems and their use in controlling airborne contaminants generated by industrial processes is the topic of this presentation. Title 29 Code of Federal Regulations (CFR) 1910.1000 (e) states, "To achieve compliance with paragraphs (a) through (d) of this section administrative or engineering controls must first be determined and implemented whenever feasible. When such controls are not feasible to achieve full

compliance, protective equipment or other protective measures shall be used to keep the exposure of the employees to air contaminants within the limits prescribed in this section."

Unfortunately, some materials used in industrial operations are not listed in Occupational Safety and Health Administrations' (OSHA) Permissible Exposure Level (PEL) tables in 1910.1000 nor are they listed in the Threshold Limit Values (TLV) and Biological Exposure Indices published by the American Conference of Governmental Industrial Hygienists (ACGIH). The industrial hygiene research community must establish exposure limits for advanced composite materials and related processes. An industrial ventilation system is usually installed when the contaminant is known and the established TLV is exceeded. In the Navy, these controls are initiated when the exposure level reaches an "action level" of one half the TLV or PEL. With advanced composites it is prudent to install industrial ventilation systems and use personnel protective equipment for suspect chemicals even though the TLV or PEL is not established or, as in some cases, when no accepted method is available to analyze for the material.

Our work at NEESA supports the end user of composite materials, usually in maintenance and repair facilities and laboratories.

The Navy uses two design resources, "Industrial Ventilation, a Manual of Recommended Practice," published by ACGIH and a military handbook, "Industrial Ventilation Systems", MIL-HDBK-1003/17. The ACGIH manual takes the user through industrial ventilation basics, various industrial ventilation components, and addresses hood design for many processes. The military handbook gives design criteria for specific industrial processes common to the military. The military handbook addresses fiber reinforced plastic repair processes which may be similar to some advanced composite repair processes. But none of the sample processes in either publication addresses advanced composite materials specifically, therefore, professional judgment is needed.

An industrial ventilation system exhausts contaminated air and simultaneously replaces it with clean air using mechanical equipment. In addition to evacuating contaminated air from the room in which the processes occur, the industrial ventilation system maintains a negative pressure in the workroom to prevent contaminated air from migrating to unprotected adjacent rooms or outdoors. The important concepts in this paragraph are discussed in this presentation.

EXHAUST AIR SYSTEMS

First, exhausting contaminated air is obvious. After all, that's what people think of when you say industrial ventilation. You can feel the airflow, often hear the fan, and sometimes see the air patterns in a dusty room or in a process using hot materials. I'd like to address some basic exhaust system design concepts.

Remove the Worker from the Contaminant

Enclose the operation whenever possible.

Use robotics, where economics allow, in assembly plants and machine shops where the product is the same size and shape. Navy maintenance and repair facilities receive a wide range of products. Therefore, robotics are generally not suited to our operations.

Repair small components in ventilated glove boxes. Workers don't like glove boxes because the view is distorted and they can't get "into" or close to their work. The boxes are designed for the average male worker. For the shorter or taller-than- average worker, ergonometrics enters the picture.

Control contaminants at the source using tools with low volume, high velocity (vacuum) systems on grinders, buffers, etc. However, the extra exhaust line makes maneuvering about the shop difficult especially if the workers are also required to wear air-line respirators.

Design the System Using the Appropriate Method

Design the ductwork using an ACGIH balanced method instead of depending on blast gates or dampers to balance the system in place. When blast gates are used, workers adjust the dampers and throw off the balance elsewhere in the system.

The ACGIH manual compares the advantages and disadvantages of the two design methods. Generally, designing with blast gates is more flexible especially if some processes on the same line are intermittently used. The static pressure balance method is generally more energy efficient. Furthermore, air volumes cannot be altered by unauthorized personnel so the volume flow rate is constant. In "Fundamentals Governing the Design and Operation of Local Exhaust Systems" Standard Z9.2, the American National Standards Institute (ANSI)

recommends that the static pressure balancing method be used when highly toxic materials are used, but ANSI doesn't quantify the term highly toxic

Separate the Processes

Separate vapor producing processes from dust producing processes. Maintenance shops are often designed as an afterthought and squeezed into existing spaces. Consequently, space is at a premium. The thinking is: "Workers can't be in two places at the same time. Why not use the lay-up hood to do the grinding and buffing?" The reason is: there are two different types of exhaust streams, a dust and a vapor.

Mixing the two air streams increases the potential for explosion. Some composite processes off-gas solvents. When the ductwork runs through cooler rooms some vapors may condense and pool. Dust in a vapor control system could aggravate a fire, should one occur.

Air pollution control may be compromised. Dust filtration is usually a dry process. Vapors will alter filtration efficiency. In heavily regulated locations the loss of a few percentage points of air cleaning efficiency may be the difference between a fine and compliance. Air pollution control for solvent generating processes may include afterburners or carbon adsorption, designed for wet processes. Dust and fibers may plug the system.

Apply Capture and Transport Velocity Correctly

Recognize the difference between capture velocity and transport velocity as a design and testing parameter. Many people use capture velocity to evaluate the industrial ventilation system. They use a fixed value for all similar processes. For example, all paint booths must have a capture velocity of 150 feet per minute (fpm). This is a good start. However, ACGIH defines capture velocity as, "The velocity at any point in front of the hood necessary to overcome opposing air currents and to capture the contaminated air by causing it to flow into the exhaust hood."

When man cooling (pedestal) fans are used, or doors and windows are opened, cross drafts are generated. The general rule of a 150 fpm capture velocity is useless. Velocities of 300 fpm may be needed to overcome cross drafts and get contaminants to flow into the hood. However, high capture velocities are not the recommended solution to cross drafts. Instead, put baffles on the hood to help direct the airflow. Physical and administrative

controls should be initiated to keep the doors and windows closed. Physical controls may include automatic door closers or nailing the windows shut.

Hoods with high capture velocities can endanger the worker in an unexpected manner. More is not better. The high velocity air stream flows around the workers back, forming eddies and a low pressure zone immediately in front of the worker. This low pressure area allows air to stagnate and the worker breaths contaminant-laden air. Thus, we have defeated the purpose of providing engineering controls.

Transport velocities are duct flow rates. Based on experience, we have learned that material does not settle in the ductwork.

Avoid common exhaust system design errors:

1) Inappropriate hoods for the process or locating them too far from the contaminant source do not provide protection. Furthermore, they give the worker a false sense of security.

2) Sharp duct entry angles which are greater than 30 to 45 degrees prevent smooth airflow, generate eddies, and increase resistance in the ductwork. In dusty operations particles accumulate in these areas.

3) Tight elbows which are either mitered, have a radius of curvature of less than two, or have an aspect ratio of less than two cause problems discussed in 2 above.

4) Abrupt duct expansions and contractions greater than 15 degrees cause problems discussed in 2 above.

5) Fan system effects caused by air system elements (elbows, coils, filters, dampers etc.) within five to ten duct diameters of the fan inlet and outlet introduce turbulent and asymmetrical airflow into the fan. Manufacturers report fan performance data based on tests using long straight duct at the fan inlet and outlet. If overlooked when specifying the fan, these system effects result in lower than expected flow rates and higher operating pressures.

6) Short exhaust stacks or locating stacks near the supply air intake allow contaminated air to be drawn back into the building.

REPLACEMENT AIR SYSTEMS

A properly designed replacement air system is one of the most critical but often poorly designed components in an industrial ventilation system. The replacement air volume should be designed to maintain a negative pressure between 0.05 and 0.10 inches water

gauge (in. WG). Modulate the replacement air fan to accommodate adjustments in airflow. Filter the replacement air to protect the processes and mechanical equipment. Replacement air should be delivered to create a "ram" of low velocity air moving at about 50 fpm across the room. This system must be designed in conjunction with the exhaust air system and not as an afterthought. I'd like to address some basic replacement air system design concepts.

Maintain a Slight Negative Pressure in the Work Room

To keep contaminants in the work room we recommend the 0.05 to 0.10 in. WG. relative to atmospheric pressure or the design pressure of the adjacent rooms. Higher negative pressures make doors difficult to open and can create a safety problem when doors slam shut. When high negative pressures occur workers tend to prop the door open--there goes the negative pressure balance. High negative pressures also waste energy because the exhaust fan has overcome the additional resistance.

Modulate the Replacement Air Volume

Modulate the replacement air to the entire room with a variable air volume system. In large workrooms where workspaces (hoods) are intermittently used, the replacement air fan must be modulated. When work pieces are moved in and out of the room while the exhaust fan(s) are operating, replacement air volume must be reduced because air flows through the open door. Without a reduction in mechanically supplied replacement volume, the increased airflow into the room may create a positively pressurized balance. The replacement and exhaust fan controls must be tied together by a control system.

Distribute the Replacement Air Evenly

Replacement air delivery should be spread over the whole ceiling or from a wall opposite from the hood(s). If all the hoods are located on one wall, then a wall mounted replacement air design may be acceptable. When work stations are located all over the room, a ceiling mounted replacement air design is recommended. Whenever the velocity in a room is above 50 fpm, it can be detected by most people. Velocities above 50 fpm begin to create turbulence when they impinge on objects in the airflow. You don't want employees working in the contaminated air stream from another hood. Equipment and work pieces in storage may also block airflow across a room. Completed and next-in-line work pieces are

often stored in the workroom during operations where employees have to complete an extensive decontamination process to exit the room.

Some replacement air distribution systems, particularly diffusers and grate-type delivery systems, contribute to turbulence in the room by concentrating the airflow in a few areas. Supply air can be "thrown" at high velocities for a considerable distance.

We recommend supplying replacement air through a plenum with a face made of perforated plate. The plenum should extend over the whole wall or ceiling. The perforated plate is specified based on the required volume, the plenum area, and a flow through the 3/8 inch holes of 2000 fpm. Rooms with ceilings above 15 feet can be supplied by a perforated duct as long as it spans the shop.

Temper the Replacement Air

As a general rule, we recommend that replacement air be tempered using a winter design temperature of 55° F (minimum) and a summer design temperature of 78° F (maximum) and conditioned at 50 percent relative humidity. Deliver heated replacement air about ten feet from the floor if possible. Controlling temperature and humidity is critical in shops where employees are required to wear impermeable clothing and heat stress may occur. The process itself may also dictate workspace temperatures. There are heating and cooling guide lines in "Facility Planning and Design", MIL-HDBK 1190.

Use Only 100 Percent Outside Air

Do not recirculate contaminated exhaust air. Our current air pollution control technology is not efficient enough to use recirculating air systems for toxic chemicals. An energy saving heat exchanger may be considered. However, the contaminated exhaust air stream and clean supply air stream must never be in direct contact with each other.

Supply Air to the Room Using a Mechanical System

Finally, replacement air should be mechanically supplied to a room I'm sure you have seen louvers in a door or wall which allow air into the room. Naturally supplied replacement airflow cannot guarantee a negative pressure in a room. The exhaust fan in a naturally supplied system has to pull fresh air through the louvers in addition to exhausting contaminated air at the hood. Less energy is required to blow (replace) air into a space than

to pull (exhaust) air from the space. Relying on naturally supplied air may reduce first or capital costs, but contaminant control is compromised.

SYSTEM MAINTENANCE

Another important design consideration is ease of maintenance. Listed below are several ideas that can be incorporated into a design to make the maintenance job easier.

1) Provide screens or perforated plates above the slots to keep paper towels, rubber gloves, aluminum foil, sandwich bags, and other debris from becoming sucked into the system. Debris caught on the blades can cause fan misalignment and unnecessary noise. Debris gets caught on dampers and blast gates.

2) Ventilate the waste cans. Rags, wipes, waste mixing containers, etc., may contain contaminated materials that add to the chemical burden in the room if not properly ventilated.

3) Provide cleanout doors for the ducts in dust laden operations. ACGIH gives guidance on locating the cleanout doors.

4) Mount fans on the roof. In addition to being unsafe, fans mounted in the rafters contribute to the noise in the shop. If you must locate the fans in the rafters, provide catwalks all the way around the unit.

5) Provide accessible controls and test ports.

6) Provide gauges connected to sensors at the entrance to the workplace so workers can monitor the system performance on a day-to-day basis. Mark acceptable ranges in green and the unacceptable in red. Train the workers to identify problems early and to periodically calibrate the gauges.

7) Isolate the fan by providing vibration and damping to reduce noise and prevent shaft misalignment.

8) Provide a protected space to change both replacement air and exhaust air filters and maintain the equipment, e.g., for large systems, a penthouse. Make sure there is room to pull the filters out of the housing.

9) Locate the mechanical room lighting where bulbs can be easily changed.

10) Attach a set of operating instructions and baseline performance data in a zip lock bag attached to the fan housing. This is in addition to the sets left with the public works and the industrial hygiene offices.

One final comment on maintenance. We do not recommend installing the fans and air pollution control equipment in a basement or on a mezzanine. We have seen several shops where replacement scrubbers and fans must be fabricated and installed on site. There is no room for a crane or fork-lift to move off-the-shelf replacement equipment into the available space.

We recommend that all designers go out to "their" shop. Talk to the sheet metal contractor, mechanical contractor, and equipment installer. Talk with the operators during plant start-up and after the shop has been in use for at least a year. It's a humbling experience.

PERFORMANCE OR ACCEPTANCE TEST

An important aspect of the ventilation system is the acceptance or performance test. Acceptance testing is performed on a new ventilation system to determine that the system operates as designed. If design is inadequate, an acceptance test cannot provide improved worker protection. Performance testing uses the same procedure to establish the current status of an existing system.

It is not a good idea to have the installing contractor perform the acceptance test, although that's how most contracts are written. In reality, it is usually the sheet metal contractor or the general construction contractor who performs the acceptance test. We have seen "dry lab" test acceptance results where all test results were divided by a common denominator based on the size of the hood. Luckily the Resident Officer in Charge of Construction was suspicious of the testing group and challenged them.

Periodic system performance testing is required by OSHA for several processes, including plating and asbestos rip-out facilities, after the system is on line. Navy regulation OPNAVINST 5100.23B requires periodic testing of all ventilation hoods. ACGIH and ANSI Z9.2 also recommend periodic testing. Periodic is generally interpreted as annually but may be earlier if the contaminant is highly toxic, the industrial ventilation control is marginal, the personnel/area samples indicate a change in control, or the process changes.

ACGIH recommends hood suction measurements using a Pitot tube and manometer as the preferred method for periodic testing. The velometer only indicates capture velocity in and around the hood.

Hood pressure readings, taken with a Pitot tube and manometer, vary as the square of the volume and velocity. Pressure testing is a fairly sensitive indicator of velocity and volume changes in the system. A 20 percent difference in static pressure indicates a 10 percent diffe-ence in volume flow rates. The Pitot tube and manometer are not effected by cross drafts in the room.

TRAINING

At NEESA we present a five day industrial ventilation design class geared for industrial hygienists and mechanical engineers working with military-related processes. There are several universities and at least one private contractor providing similar information. These classes are essential for engineers and industrial hygienists performing design review and monitoring design contracts. It is recommended for industrial hygienists performing hood evaluations.

CONCLUSION

Finally, we find that industrial ventilation, as opposed to administrative controls which are an option in 29 CFR 1910.1000, is a more consistent form of worker protection in the industrial settings. However, you can give the workers a false sense of security by providing a poorly designed ventilation system with haphazard maintenance. Even with a well-designed and well-maintained industrial ventilation system, additional respiratory protection may be required if you cannot guarantee that the industrial ventilation system fully protects the worker.

REFERENCES

1. Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1979, American National Standards Institute, Inc , New York, NY 1980.

2. General Industry Standards, Title 29, Code of Federal Regulations, Part 1910.

3. Industrial Ventilation, a manual of recommended practice, The American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 19th edition, 1986.

4. Industrial Ventilation Systems, Military Handbook 1003/17, Naval Energy and Environmental Support Activity, Port Hueneme, CA, 1986.

ANNOTATED BIBLIOGRAPHY

Ventilation System Testing,Industrial Ventilation, Committee on Industrial Ventilation, P.O. Box 453, Lansing, MI 48902.

Caplan, Knowlton J. and Gerhard W. Knutson, "Influence of room air supply on laboratory hoods", American Industrial Hygiene Association Journal, vol. 43(10), pages 738-746, 1982.

ASHRAE Fundamentals, American Society of Heating, Refrigerating, and Air Conditioning Engineers, Atlanta, GA, 1985.

ASHRAE Equipment, Same as number 3. Chapter 3, Fans.

Clarke, John H., "Air Flow Around Buildings", Heating, Piping and Air Conditioning, pp. 145-154, 1967.

Whitehead, Lawrence William, "Planning considerations for industrial plants emphasizing occupational and environmental health and safety issues", Applied Industrial Hygiene Journal, vol. 2, no.2, pp. 79-86, March, 1987.

Goldfield, Joseph, "Contaminant reduction: general vs. local exhaust ventilation", Heating/Piping/Air Conditioning, pp. 47-51, February, 1985.

Koshland, Catherine Preston and Michael G. Yost, "Use of a spreadsheet in the design of an industrial ventilation system", Applied Industrial Hygiene Journal, vol.2, no. 5, pp. 204-212, September 1987.

Goldfield, Joseph. "Elements of fan selection for industrial ventilation", Heating/Piping/Air Conditioning, February 1987, pp. 53-58.

Air Movement and Control Association (AMCA), 30 West University Drive, Arlington Heights, IL 60004, produces a newsletter, "TECHSPECS".

AMCA Fans Application Manual, Part 1- Fans and Systems, AMCA 201; Part 2-Troubleshooting, AMCA 202; Part 3- Field Performance Measurements, AMCA 203, 1985.

AMCA Air Systems, Publication number 200.

Chicago Blower Corporation 1675 Glen Ellyn Road, Glendale Heights, IL 60139 produces a series of five pamphlets titled "A Basic/Advances Course in...". They also produce a pamphlet called "Fan Doctor".

The Sheet Metal and Air Conditioning Contractors' National Association, P.O. Box 70, Merrifield, VA 22116 also produce standards and relevant publications.

COMPOSITE FIBER FIELD STUDY: AN EVALUATION OF POTENTIAL PERSONNEL EXPOSURES TO CARBON FIBERS DURING THE INVESTIGATION OF A MILITARY AIRCRAFT CRASH SITE

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ABSTRACT

The increasing use of carbon-epoxy composite material on various types of aircraft has increased the need for information on, among other matters, the hazard presented by particles of this material. Data needed for hazard evaluation (to characterize the potential exposure) includes the nature and quantities of particulate released by manufacturing and maintenance techniques, as well as from incidents where this material is subject to both high-impact and temperature conditions as would likely occur during an aircraft mishap. This paper addresses the latter scenario and focuses specifically on release of and exposure to carbon fibers.

On 13 July 1988, an AV-8B Harrier II based at the Marine Corps Air Station, Cherry Point, North Carolina, suffered a systems failure and crashed a few miles from the runway in a small clearing. An industrial hygienist from the regional Naval Medical Command was permitted to enter the crash site to collect both area and personal samples in an attempt to characterize carbon fiber release and potential exposure during clean-up operations.

Sampling was performed in accordance with the requirements of the NIOSH 7400 method. Both area samples and personal samples were collected on 0.8 μm MCEF filters using 25 mm cassettes with electrostatic extension cowls connected to Du Pont P2500A and P2500B personal sampling pumps at a flow rate of 1.9 - 2.1 liters per minute.

Background values were < 0.1 f/cc, consistent with previous work. Activities by clean-up personnel (e.g., searching through debris, preparing debris for removal, manually removing parts) resulted in eight-hour time-weighted average fiber counts less than the 3 f/cc level recommended for carbon fibers by the Navy Environmental Health Center but greater than the 0.2 f/cc asbestos standard.

Some cases of dermatitis were reported and six personnel were seen at the Occupational Health Clinic for medical surveillance examinations. No cases of asthma, breathing difficulties or other respiratory problems were reported by clean-up personnel.

INTRODUCTION

An increase in the use of nonmetallic composite materials in aircraft has increased interest in potential health effects in personnel involved in the manufacture of these materials. The recognized health effects from exposure to other types of fiber-producing materials have raised concerns that composite materials may cause similar health effects including respiratory difficulties, pulmonary fibrosis, or mesothelioma.

One potential exposure scenario requiring evaluation is the production and release of respirable airborne fibers during an aircraft accident, which causes high-impact and high-temperature degradation of composite compounds. References 1 and 2 specifically address the potential for fiber release and possible health effects of carbon or graphite epoxy compounds. These carbon or graphite composite materials are used extensively in several types of aircraft, including the F/A-18 and AV-8B Harrier II fighters.

On 13 July 1988, an AV-8B Harrier II based at the Marine Corps Air Station, Cherry Point, North Carolina suffered a systems failure and crashed a short distance from the runway. The Naval Medical Command industrial hygienist stationed at Marine Corps Air Station, Cherry Point, requested and was granted permission to sample for airborne carbon fiber during the mishap clean-up operation. The data would be added to the database established by the Navy Environmental Health Center (see references 1 and 2).

SAMPLING AND ANALYTICAL METHODS

Both breathing zone samples and area samples were collected on SKC brand mixed cellulose ester filters (25 mm, 0.8 micron pore size) in open-faced filter holder cassettes with electrostatic cowls using Du Pont P2500 sampling pumps (flow rate 1.9 - 2.1 lpm). Samples were sealed in the cassettes in the field and transported to the lab with a minimum of jostling or impact, and counted in most cases within 24 hours of arrival at the lab.

Samples were analyzed by the Naval Hospital Industrial Hygiene Division, by personnel who have maintained satisfactory levels of performance in the PAT (Proficiency Analytical Testing) program. Filters were cut in half, placed on slides and the filter matrix dissolved away using acetone and a Quik-Fix brand heating unit. Counting was done on an Olympus phase contrast microscope with a Walton-Beckett graticule. Fiber counting rules were used as dictated by NIOSH for asbestos fibers.

Tables 1 - 4 display the results for each day's sampling, including sample durations and the resultant fiber counts, reported as number of fibers per cubic centimeter of air (f/cc); those which were taken from the breathing zones of various personnel are also converted to eight-hour time-weighted averages (TWA_{8h}).

CRASH SITE CONDITIONS AND PROTECTIVE EQUIPMENT

Clean-up of the crash site was carried out during the period 14-18 July 88. Weather conditions were hot and humid, with temperatures greater than 90° F and relative humidity greater than 60 percent. Wind was predominantly from the south, with light breezes of three to four knots. Heat stress was a matter of some concern during these operations; plenty of cold drinking water was provided, however, and the area was secured when mid-day temperatures approached 98° F.

Most of the aircraft debris was contained in an oval-shaped area approximately 75 feet by 300 feet in the midst of a pine forest. After determining there was no longer a fire hazard, crash crew personnel approached the site wearing long-sleeved Tyvek® suits and full-face or half-face respirators with HEPA cartridges. To minimize fiber release, commercially available floor wax mixed with water was sprayed as a fixative on those large areas of damaged composite that were accessible.

For debris removal and site clean-up, personnel were provided with leather gloves and disposable 3M 8710 respirators, and were encouraged to keep their arms covered, if possible, despite the high heat and humidity.

Personnel actively involved in searching through debris, moving large pieces, and loading the truck were provided with Tyvek® suits, half-face rubber respirators with HEPA cartridges, goggles, and leather gloves. All personnel were advised to shower before returning home from the field and to launder all clothing separately.

The precautions described above, which are directed by the Naval Safety Center in reference (5), and the permissible exposure level recommended by the Navy Environmental Health Center of 3 f/cc as a TWA_{8h}, are based on those for handling of and exposure to fibrous glass, in the absence of more definitive toxicological data.

TABLE 1
JULY 14, 1988

SAMPLE type & #	LOCATION	DURATION in min	FIBER COUNT in f/cc	TWA_{8h} in f/cc
Area				
1	Near tail	256	< 0.010[a]	
2	Near tail	219	< 0.011	
3	Main debris south	272	< 0.009	
4	Main debris south	206	0.015	
5	Main debris east	166	0.015	
6	Main debris east	192	< 0.013	
7	Main debris west	349	0.008	
8	Impact crater	235	< 0.010	
9	Impact crater	228	< 0.010	

[a] < 0.0XX indicates best estimate when fewer than 10 fibers counted per 100 microscopic fields.

TABLE 2
JULY 15, 1988

SAMPLE type & #	LOCATION	DURATION in min	FIBER COUNT in f/cc	TWA_{8h} in f/cc
Area				
10	Impact crater	134	0.018	
11	Impact crater	160	< 0.015[a]	
12	Near wing debris	132	< 0.018	
13	Near wing debris	221	1.060	
14	Main debris north	36	< 0.066	
15	Main debris south	204	0.118	
Personal				
16	Observed searching	151	< 0.016	< 0.005
17	Searching in debris	27	6.142	0.345
18	Searching in debris	27	3.670	0.206
19	Operating heavy equipment	27	2.865	0.161
20	Operating heavy equipment	76	< 0.030	< 0.005
21	Guiding operator	34	< 0.073	< 0.005
22	Working on truck	21	6.998	0.306

[a] < 0.0XX indicates best estimate when fewer than 10 fibers counted per 100 microscopic fields.

TABLE 3
JULY 16, 1988

SAMPLE type & #	LOCATION	DURATION in min	FIBER COUNT in f/cc	TWA_{8h} in f/cc
Area				
23	Impact crater w/work	57	< 0.043[a]	
24	Impact crater w/work	56	< 1.835	
25	Main debris north	62	< 0.048	
26	Near stacked debris	89	0.692	
27	Moving tail section	42	0.694	
Personal				
28	Picking up pieces by hand	115	< 0.671	0.161

[a] < 0.0XX indicates best estimate when fewer than 10 fibers counted per 100 microscopic fields.

TABLE 4
JULY 18, 1988

SAMPLE type & #	LOCATION	DURATION in min	FIBER COUNT in f/cc	TWA_{8h} in f/cc
Area				
29	Near stacked debris	217	0.020	
Personal				
30	Working in impact crater	21	0.584	0.026
31	Moving wing	19	0.363	0.014
32	Moving wing	10	3.170	0.066

CLEAN-UP OPERATIONS AND SAMPLING RESULTS

During the first day, nine area samples were taken (Table 1); all fiber counts were substantially less than 0.02 f/cc. These values are within the range noted elsewhere (reference 3) for damaged composite material stored in a hangar. Analysis of the wreckage was initiated, but few personnel were permitted into the debris area and no major aircraft pieces were disturbed.

The next day saw more vigorous handling of the damaged composite material and more personnel movement throughout the area (see Table 2). Area sample fiber counts remained less than 0.02 f/cc except near some of the larger aircraft parts where hand searching was occurring. In these areas, fiber counts ranged from approximately 0.1 to 1.1 f/cc.

Breathing zone samples were taken of marines actively involved in tearing apart the main pieces of debris by hand while searching for electronic parts. Two samples taken during such a search, lasting about 30 minutes, had fiber counts of 3.6 and 6.1 f/cc, or TWA_{8h} of 0.21 and 0.35 f/cc, respectively. One marine spent 20 minutes positioning material on a flatbed truck; this task resulted in a breathing zone fiber count of 7 f/cc, or a TWA_{8h} of 0.31 f/cc. A breathing zone sample from the forklift driver for a single operation (moving and loading the largest piece of composite material - a wing section) yielded a TWA_{8h} fiber count of 0.17 f/cc.

The third day involved the use of shovels and rakes to remove contaminated soil as well as further moving and stacking of debris, and the loading of large parts onto a flatbed truck to be wrapped in plastic (Table 3).

One area sample near the impact crater had a fiber count of almost 2 f/cc during a busy period of digging up and removing parts from the crater, while two area samples near stacked or broken debris had 0.7 f/cc.

One marine monitored for almost two hours during the morning, while picking up debris by hand, had a TWA_{8h} fiber count of 0.16 f/cc. Work done on the last day (no work was done on 17 July) was similar to that done on 16 July (Table 4).

An area sample near debris that had been stacked up awaiting removal had a fiber count of 0.02 f/cc.

A breathing zone sample from a marine working in the crater gave a TWA_{8h} fiber count of 0.03 f/cc. A wing section was removed from between two trees, wrapped in plastic and placed on a truck; this resulted in TWA_{8h} breathing zone fiber counts of 0.02 and 0.07 f/cc for the two personnel involved.

DISCUSSION

Both initial observations and sampling results support the concern regarding the potential for exposure to carbon/graphite fibers of personnel engaged in damage control, fire suppression, and clean-up operations where structures using composites are involved. A large amount of fibers had been released from the wreckage and distributed around the site. Moving or shifting damaged composite material resulted in significant airborne concentrations of fibers, as did the removal of contaminated soil. All personnel were aware that this situation posed an uncertain degree of hazard, and were careful to have gloves and disposable respirators available.

The fixative appeared to be moderately successful in reducing the generation of airborne fibers. The floor wax-water mixture produces a sticky solution that dries to a thin, tacky film that the crash crew members find quite satisfactory. Fiber counts might well have been higher had the fixative not been used.

A factor which may have resulted in an underestimation of airborne concentrations is an electrostatic effect between the carbon fibers and the plastic material of the sampling cassettes. While the sampling protocol used was basically the same as recommended by reference 4, it is possible that this effect might have caused a significant percentage of the fibers sampled to adhere to the sides of the sample cassettes, leading to an underestimate in the fiber count.

Fibers were counted using the method specified for asbestos. While interfering fibrous materials were present, they were not numerous nor did they present the morphology described in reference 2 as defining a man-made fiber, i.e., straight fibers with clean-cut edges.

TWA_{8h} values were calculated for each person from the data obtained during the sampled time period (see Tables), and assume no exposure for the rest of the day. For some of the shorter sampling periods, work similar in nature to the sampled work continued to be performed by the same individual. Further calculation showed that the work which

resulted in the highest fiber counts would need to be done for three to four hours to make an appreciable change in the TWA_{8h}. Because of this simplifying assumption in the calculations and the suspected sampling problem described above, the TWA_{8h} values should be viewed as lower bound estimates of exposure to airborne fibrous material.

The squadron flight surgeon identified a dermatitis or skin rash on the forearms and lower arms of two of the involved personnel. This may have been similar to the mechanical irritation produced by fiberglass. All personnel who were actively involved in recovering debris were evaluated by an occupational health physician following the guidelines in references 1, 2, and 6 for medical surveillance. There were no reported instances of breathing difficulties or respiratory problems. Three of these personnel were smokers, and two others had previously been involved in the clean-up of a Harrier mishap in California.

CONCLUSION

A mishap involving an aircraft or other structure with carbon or graphite composite components will generate a significant number of fibers which can become airborne as a result of the clean-up process (and are probably airborne during and immediately after the mishap). Concentrations present under such conditions (i.e., mishap clean-up, and probably damage control and fire suppression actions) would be consistently greater than 0 2 f/cc as a TWA_{8h}, the standard set for asbestos fibers, but would infrequently reach the standard suggested by the Navy Environmental Health Center of 3 f/cc as a TWA_{8h}.

ACKNOWLEDGMENTS

The Industrial Hygiene Division, Naval Hospital, Cherry Point would like to thank LtCol Ricker, Head of the Accident Investigation Board and LCDR Stephen "Rocky" deVeer of the Naval Safety Center for permission to work at the site and gather this information. Special thanks go to the members of Marine Attack Squadron 203, who were conscientious and very helpful.

REFERENCES

(1) CO, NAVENVIRHLTHCEN ltr 6261, Ser 34/10209, 19 Oct 84

(2) CO, NAVENVIRHLTHCEN ltr 6290, Ser 332.1p/06513, 29 Jun 87

(3) Memo from LT Burton, NAVHOSP Cherry Point to LT Fraser, NAVHOSP Cherry Point, 12 Mar 86

(4) Silverberg, G. D. "Overview : Graphite Composite Fibers" Presentation at the 29th Annual Navy Occupational Health and Preventive Medicine Workshop,Norfolk VA, 28 Feb - 6 Mar 87

(5) NAVSAFECEN Norfolk VA 081500Z Jun 87

(6) COMNAVMEDCOM ltr 6260, Ser 242/0406, 3 Jun 87

VI. OCCUPATIONAL MEDICINE CONSIDERATIONS

CONSENSUS STATEMENT

A principal role of Occupational Medicine (OM) in the advanced composite industry is to carefully evaluate workers who have been exposed to composite materials. OM's role is not unique to composite industry but encompasses all aspects of research and development, manufacturing, and user industries.

Most of the well-established general problems of resins, hardeners, and solvents also exist with those that have composite applications; e.g., irritant and allergic dermatitis and sensory and mucous membrane irritation.

Industrial hygiene information to date indicates that composite fibers are not of a size to penetrate deeply into the lung or pose a cancer hazard. Nevertheless, potential respiratory effects should be addressed as part of medical monitoring.

Episodic exposure of greater than normal intensity to composite materials (fire, spills, resin exotherm) may occur and should be medically evaluated. These exposures should be further investigated for potential linkage to the recently described reactive airways dysfunction syndrome (RADS) (mild asthma).

Antibody levels and other immune system testing currently do not correlate with exposure or clinical illness and should be performed only as a part of a well-controlled epidemiological study.

Methylenedianiline (MDA) is a particular concern in OM. Animal data and anecdotal human data implicate this substance as a liver toxin. It is a known animal and "suspect" human carcinogen. Medical monitoring with liver function tests (LFTs) is necessary for the most frequently exposed worker. Measurement of MDA in body fluids in this case appears to be feasible and needs to be explored. Other chemicals may also require medical monitoring, but good methods have not been adequately developed.

Phenol-formaldehyde is one of the most frequently encountered resins in industry today. Laboratory testing for serum antibodies to formaldehyde is not useful for individual employee monitoring due to the lack of a clear understanding of their significance. Medical monitoring of employees exposed to phenol-formaldehyde resins should be performed. Monitoring for formaldehyde, phenol, or their metabolites is currently not useful.

An unresolved key issue is the combination of extrinsic and/or intrinsic psycho-social stressors (long work hours, cancer-phobia, misinformation from health care providers, labor-management friction, media hype) with low-level workplace irritants (odors, respiratory irritants). This combination may result in a "crisis of concern" which makes objective study of the issue impractical. When this results in anxiety and depressive disorders, the accompanying nonspecific symptoms create an extremely confusing clinical picture.

It is not clear whether the high prevalence of anxiety and depression seen in some composite workers is due to very low-level chemical exposure associated with sensory irritation of the respiratory tract. It is possible that sociological factors (such as fear, distrust, misinformation from health care providers, group interaction, attorney and/or media involvement, or labor-management problems) are playing a major role in producing or exacerbating these workers' symptoms. To address this concern, it is necessary to study the prevalence of anxiety and depression in a similarly exposed group of workers and matched controls in work places that are not "contaminated" by these other sociologic factors. Carefully designed epidemiological studies are needed if one is to address the influence of such sociologic factors.

RECOMMENDATIONS

Medical monitoring should encompass the establishment of an employee baseline exam and incorporate the acquisition and review of periodic medical evaluation data. The function of such monitoring as a tool to provide early identification and prevention of occupational illness currently has technical limitations; nevertheless, such monitoring for workers engaged in composite fabrication and/or rework can be clinically useful and serves to establish a good relationship with the worker and promote early contact when problems do arise.

While medical monitoring is a very valuable tool, the primary method of preventing occupational illness in the composite industry should be the control of chemical exposures in the workplace using good industrial hygiene practice such as:

a. Substitution of selected chemicals with less toxic substances.

b. Engineering controls such as process enclosures and local exhaust ventilation.

c. Administrative controls such as limiting exposure time.

d. Use of personal protective equipment for the eyes, skin, and respiratory system.

e. Employee education and training.

Health and safety professionals must be involved in impact analysis for any new or unfamiliar chemical at the research and concept stages rather than just the manufacturing or post-manufacturing stages. Toxicity assessments, industrial hygiene measures, and medical monitoring protocols can thus progress in parallel with industrial research and development.

A CASE REPORT ON PULMONARY EFFECTS IN TWO INDIVIDUALS EXPOSED TO PYROLYSIS DEBRIS FROM A COMPOSITE AIRCRAFT MISHAP

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ABSTRACT

Two of four men on site between 8+ and 11+ hours after an F/A-18 crash presented with complaints of markedly reduced exercise capacity, first noticed a few days after the above exposure. A background explanation of pulmonary anatomy, pathophysiology and function testing is presented, followed by the case reports. In both individuals there was an abnormality in the alveolar/arteriolar gradient. Which raises the questions, could alveolar damage have been caused by cadmium or hydrogen sulfide adsorbed onto pyrolyzed graphite? Both demonstrated improvements of approximately 1/2 liter in Forced Vital Capacity (FVC) six months following the accident. In one of them there was an abnormal one second forced expiratory volume (FEV1) which improved 30 percent back to normal over six months; a markedly reduced exercise capability and a positive histamine challenge test The symptoms and pulmonary testing in the person were consistent with the Reactive Airway Dysfunction Syndrome (RADS).

I conclude that exposure to compound pyrolysis debris from a high tech aircraft may result in heightened airway reactivity in certain susceptible individuals. The very unique circumstances of the exposure presentation are stressed. Independent suggestions are made regarding personnel protection during fire fighting and fire overhaul of high tech aircraft mishaps.

INTRODUCTION

Two men, one the sheriff of Catalina Island and the other a member of the Los Angeles County Sheriff's Department Search and Rescue (SAR) Team, presented to two different university occupational medicine clinics with complaints of severely diminished exercise capacity first noted a few days after being exposed to dust, smoke and fumes, on site for three hours starting approximately 10 hours after an F/A-18 crash. There were two other apparently asymptomatic county employees on site during the same time. I'm going to

first provide a basic description of lung anatomy, lung pathogenesis, and pulmonary function testing in order to provide an adequate background prior to the case presentations. The discussion section deals with my inquiries and overview of literature to attempt to explain the symptoms and pulmonary function findings demonstrated in these two men. Next, I'll conclude the case presentation segment of my discussion by giving my assessment of these cases and conclusions relative to exposure to the pyrolysis debris of the aircraft. Finally, I'll make overall recommendations regarding personnel protection during fire fighting situations.

Figure 1 is a schematic of the lung anatomy. On this figure after the trachea divides at the hilum into the left and right main stem bronchus are a series of divisions of the bronchi. Actually, these divisions are of nine orders, so there is quite a bit of branching that goes on. The bronchi are smooth, muscle lined cylinders which do contain cartilage. The next airway passage are the bronchioles which are also smooth, muscle lined, much smaller cylinders, and cartilage free. The bronchi, bronchioles, and the terminal bronchioles which lead into the respiratory units comprise the conducting airway system of the lungs. In severe airflow abnormalities, the bronchi constrict. It is more common, even in less severe breathing abnormalities, for the bronchioles to constrict as they are the most reactive of the conducting airways.

The functional air exchange unit of the lungs, the respiratory unit, or the acinus, is next demonstrated. It is composed of respiratory bronchioles, alveolar ducts, and alveoli. In the alveoli the air exchange between the lungs and the circulation takes place. Oxygen diffuses from the alveoli into the capillary circulation of the pulmonary blood system, and carbon dioxide moves from the pulmonary circulatory system into the alveoli to be exhaled In responding to foreign substances, the lung has a limited number of acute reactions. I will discuss the three relevant responses to foreign toxic substances. The first is an irritant or an inflammatory effect, and can involve either the conducting airways with broncho-constriction, or the acinar units, an alveolar effect, which can be as severe as causing pulmonary edema Which type of effect occurs has to do with the inherent toxicity of the particle, fume, or vapor inhaled, and the solubility of this particle in tissue. The size and polarity of the particle determines how far into the respiratory tract it reaches. In the case of fibers, the principal determinants are fiber diameter and change.

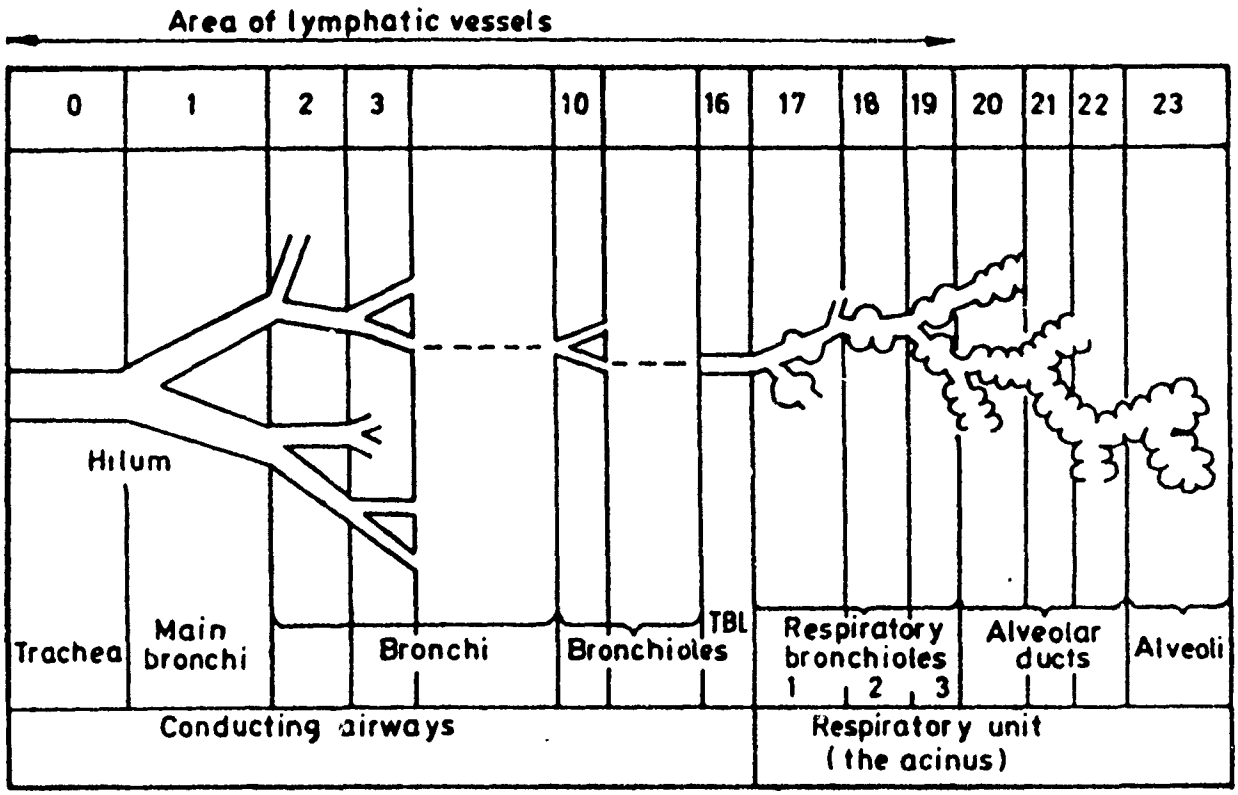


Figure 1. Conducting airways and respiratory unit (not to scale). Figures at the heads of the columns indicate the approximate number of generations from trachea to alveoli. (From Parker[5], 1982)

Another response that the lung has is an allergic response. Generally, this allergic response involves circulating immune complexes. When a foreign substance is inhaled repeatedly by the lungs eventually this substance results in the body creating antibodies which react with a portion of this substance thus creating immune complexes.

These immune complexes stimulate mast cells and reactive molecules from within the cells lining alveoli to release bradykinen and other substances which possess vasospastic quantities resulting in bronchospasm (that is constriction of the bronchi). Asthma resulting from repetitive isocyanate exposure is a classic example of this allergic reaction.

Finally, in the case of certain rare metals and toxic organic chemicals as well as strong acids and bases, the lung can have a cytotoxic reaction which involves a certain amount of cell death and the transudation of fluid across the cell membrane into the alveoli and/or breathing passages. In severe inhalation exposures, this reaction can result in pulmonary edema and death.

The range of lungs' responses to repetitive foreign insults is even more limited than its acute response repertoire. These include either a fibrogenic reaction, either within the bronchioles as in silicosis or acini as with asbestos; destruction of acinar units as with emphysema - cigarette smoke or a malignant neoplastic reaction from exposure to toxic cancers initiator/promoters. Fibrosis is the result of cell injury, cell death, and scarring. Certain substances such as benz-a-pyrine or asbestos have the capability of inducing malignant transformation in pulmonary cells with resulting cancer formation with a latency period between ten and forty years.

Pulmonary function testing, like the lungs' reactions to foreign substances, is a non-specific way of evaluating lung pathology. One problem in early assessment of lung disease, especially those caused by a variety of dust, is that the major damage occurs in the bronchioli or acinar units, whereas the most commonly used test of airway function, as well as the most standardized test of airway function, involve abnormalities in the large airways.

There are five types of pulmonary function tests that are pertinent to this case report. The first two: spirometry and bronchial provocation challenges, both specific and non-specific are tests that mainly measure airflow abnormalities. The latter three tests of pulmonary function: diffusing capacity of carbon monoxide (D CO), arterial blood gas (ABG) determination, and maximal exercise testing with concurrent ABG measurement can reflect alveolar abnormalities which often result from oxygen diffusion problems. In order to

understand spirometry, Figure 2 is a simple physiologic schematic of respiratory volume nomenclature. Title Volume (TV) is the normal volume of air moved into or out of the lung when breathing. Forced Vital Capacity (FVC) is the volume of air that is moved in the excursion of the maximum inspiration to the maximum expiration. The upper part of Figure 3 demonstrates the nomenclature of the most commonly used pulmonary function test, that of the spirogram. The two most common measures are that of the forced vital capacity, which I've already defined, and the forced expiratory volume in one second (FEV1), which is the amount of air moved in the first second expiration.

The FEV1 is a somewhat sensitive indicator of chronic obstructive lung disease and is also abnormally low in acute bronchospastic episodes that is, asthma. Other more sensitive, but also less specific measures of airflow volume, are the forced expiratory flow in mid-cycle-- FEF 25-75 -- and forced expiratory flow, end cycle -- FEF 75-85. These tests are very sensitive in detecting early abnormalities of the lung airflow and correspond to bronchiolar constriction. Their overall significance, relative to physical symptoms, exercise tolerance, and association with further functional loss is less clear. The pulmonary function test with the recording of FVC and FEV1 is the only test whose performances are mandated for medical surveillance when individuals are exposed above the action level.

The second kind of spirometry test, which looks at bronchial function, is that of bronchial provocation. The most commonly used tests are non-specific in which an irritating agent is inhaled in varying concentrations. This agent can be methacholine, or histamine, or more recently, cold air has been used. Figure 4 is an example of this kind of test in a jewelry fabricator complaining of shortness of breath and wheezing after being exposed to fine shell dust and a variety of paint and plastic resins. Note that in this case there was a positive methacholine challenge test to a mid-range dose of methacholine resulting in a 34 percent diminution in the FEV1.

More commonly now, people are beginning to expose people directly to agents felt to be the specific cause of occupational asthma. Obviously, in the case of our two patients, such tests would be impossible to orovide, due to the uncertainty of exact pyrolysis product composition.

The first test used as an early indicator of acinar functional unit damage is that of D CO. Abnormal D CO can imply loss of lung units, loss of surface area, anemia, loss of capillary bed such as would occur in vasculitis or recurrent pulmonary emboli or diffusion

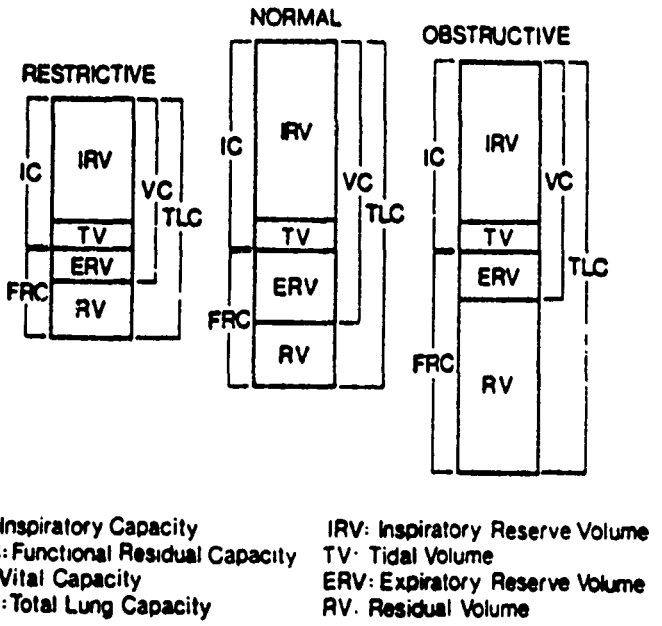


Figure 2. Lung volume nomenclature (From ALA-ATA[1]).

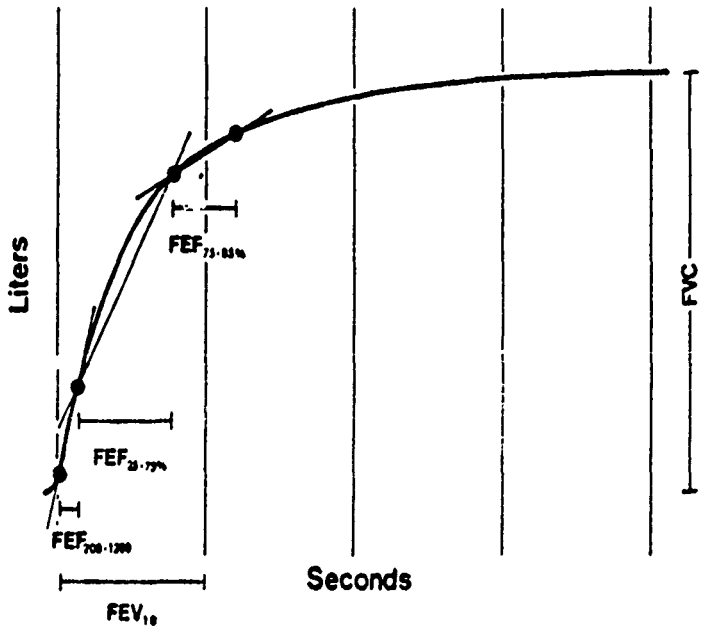


Figure 3. Pulmonary function testing -- standard flow volumes (From ALA-ATA[1]).

BARLOW HOSPITAL
PULMONARY FUNCTION LABORATORY

METHACHOLINE INHALATION CHALLENGE

COLUMN 1 CONDITION SCREEN	FVC (Liters)	FEV1	%FEV1	COLUMN 2 CONDITION	FVC (Liters)	FEV1	%FEV1
BASELINE	3.47	2.92	100	2.50 mg/ml	2.76	2.06	70
CONTROL	3.53	2.90	99	10.0 mg/ml	(Level Not Used)		
[illegible] mg/ml	3.49	2.84	97	25.0 mg/ml	(Level Not Used)		
[illegible] mg/ml	3.47	2.76	94	BRONCHODILATOR	3.55	2.86	97

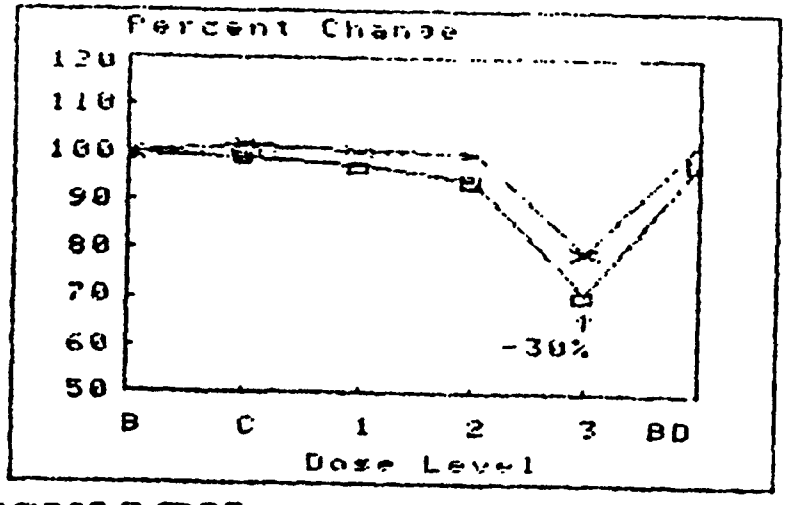
ALL DOSE LEVELS TESTED AT 2 MINUTES --- BRONCHODILATOR TESTED AT 5 MINUTES

DOSE LEGEND

B=BASELINE
C=CONTROL Pre-Diluent Only
1= 0.625 mg/ml
2= 0.25 mg/ml
3= 2.50 mg/ml
BD=Bronchodilator

PFT LEGEND

FVC= --1---
FEV1= --[]--
BASELINE= .....



IMPRESSION:

A HYPER-REACTIVE AIRWAYS RESPONSE TO METHACHOLINE INHALATION CHALLENGE TEST
AS INDICATED BY A 30% FALL IN FEV1 AT THE 2.50 mg/ml METHACHOLINE CONCENTRATION.

Figure 4. Example of positive methacholine challenge test.

block, which is seen in pulmonary edema. This is the only other test that has been employed at all in medical surveillance. It is occasionally used when screening for early signs of asbestosis.

The final two tests of pulmonary function are somewhat sensitive indicators of alveolar abnormalities. One of these is the commonly used ABG test which is helpful in determining the acid/base and oxygenation status in acutely ill patients. The other test looks at the gradient between the oxygen in the blood and the calculated oxygen content of the alveoli (A-a) O_2. Generally, this gradient is equal to approximately one quarter the age in years for a normal person. That is, for a 40-year-old person, the gradient would be ten millimeters of mercury. Moreover, with peak exercise, this gradient would not be expected to increase by more than 50 percent. Although this is a sensitive test of pulmonary function, the significance clinically is not clear in cases of small deviations from normal as this coefficient of variation for (A-a) O_2 is approximately 20 percent (Morgan and Seaton, 1984).

RESULTS

With that introduction out of the way, I can now move on and present the case of these two men. On 17 June 1984 an F/A-18 full of fuel crashed during night operations on San Clemente Island. In all, 15 acres of land and one goat were burned. These men were on site for three hours, starting approximately 10 hours after the plane crashed. Important things to note are that there were no acute symptoms of any kind when they were on site, and that predominant inhalation exposure consisted of the grapnite debris, which certainly would have at this time consisted of the majority of the respirable debris present. There was some wind and for a portion of time low-flying helicopters, which no doubt kicked up these debris and environmental dust. There was also (most likely) some exposure to some environmental smoke and fumes as there were some metal portions of the craft still smoldering. Symptoms were noted a couple of days later: in one individual, Case 1, the 39-year-old sheriff of Catalina Island, noted his exercise capacity dropped from 20 miles to 1-2 miles, and the other individual, Case 2, a 35-year-old L.A. Count Sheriff Department's Officer, noted that his exercise capacity dropped from 10 to 4 miles.

Occupational history for both men was negative for significant prior exposure. Smoking history is as follows: Case 1 is an ex-smoker who hasn't smoked in six years, although he does have a 12 pack/year history. Case 2 is essentially a non-smoker.

Social history is important. Case 1 is in world class athletic shape, participating in marathons and extended marathons. Case 2 was a member of the L.A. County Sheriff Department's Search and Rescue Unit for five years, was in tremendous physical condition, as was demanded by his position.

Past medical history was negative for asthma or allergies, family history is also negative for asthma and atopic disorders. Physical exams were normal, complete blood counts (CBCs) were normal. Chest x-rays done at the time of the clinic visits, and also when Case 2 presented to emergency room three days after this crash incident, were normal. Resting arterial blood gases, drawn on the same individual during this emergency room visit, were also normal.

Pulmonary function tests are now discussed. Case 1 had spirograms done in August and September of 1984 and the end of January 1985. Case 2 had spirograms done in August and October 1984 and in March of 1985. Figure 5 and Figure 6 review these PFT's. Inhalation challenge tests were performed on both men. Case 1 received a histamine challenge test, which was positive, showing a diminution of 33 percent over baseline in his FEV1. Case 2 received a methacholine challenge test which was negative. Exercise tests, with indwelling arterial lines, for both men reveal an increase in the (A-a) O_2 gradient. In Case 1, it was 23 millimeters of mercury, and in Case 2, it was 19 millimeters of mercury. In both men we would expect the gradient to be no more than 10. The energy expended in Case 1, probably the better conditioned of the two individuals, is only nine METS. The energy expended in Case 2 is quite high, 20.8 METS (multiple of resting metabolic state such that if resting O_2 consumption is 250 ml, an O_2 consumption of 1 liter is 4 METS). This is consistent with his superb conditioning.

In summary, we have two men, both with (A-a) O_2 diffusion gradient abnormalities when exercising and with improving PFT's -- both individuals demonstrated a 500 cc improvement in FVC. Case 1 also demonstrated a 900 cc improvement in FEV1 and had an abnormal histamine challenge test.

DISCUSSION

These abnormalities really can be broken into two compartments, that of possible alveolar damage, as evidenced by the increased (A-a)O_2 gradient and that of abnormal air-flow, as evidenced by the various spirometry abnormalities which appeared also to affect

	PRED	8/20/84	1/31/85
FVC (% PRED)	4.9L	4.5L (91)	5.0L (102)
FEV1 (% PRED)	3.8L	3.0L (79)	3.9L (102)
FEV1/FVC (%)	76	66	77
FEF 25-75 (L/Sec)	4.0	1.4 (36)	3.2 (77)

Figure 5. Pulmonary function results (Case 1)

	PRED	8/21/84	3/28/85
FVC (% PRED)	5.2L	5.6L (103)	6.1L (118)
FEV1 (% PRED)	4.0L	4.0L (100)	4.3L (109)
FEV1/FVC (%)	77	71	71
FEF 25-75 (% PR)	4.2L	2.7L (65)	2.7L (65)

Figure 6. Pulmonary function results (Case 2).

Case 1's exercise capability. Although there is a temporal link of symptoms with exposure, it would be far more satisfying to identify an agent or agents that correspond with the two individuals' pulmonary function abnormalities. The only agents that I am aware likely to be present in an aircraft that can cause alveolar type problems, that is, pneumonitis/mild pulmonary edema syndrome, would be oxides of the metals of cadmium, cobalt, and beryllium. The most toxic of these, beryllium, is only present in the aircraft in a very small amount, as an alloy of the brake pads of the aircraft. Extensive phone calling allowed me to determine that a significant amount of cadmium was used in the F/A-18.

With regard to occupational asthma, suspect agents are even harder to identify. In plastics and in the paint products industry certain compounds, notably the isocyanates (MDI and TDI), phthalic anhydride, dimethyl ethanolamine and triethyltetramine, have been associated with occupational asthma. Generally, more than one exposure has been necessary. Moreover, although these agents are present in production of some plastic systems, it would be unusual to have anything but minute amounts of these compounds liberated as pyrolysis products. The plastic resin system used to bind the graphite of the F/A-18 is tetraglycidal methylene dianaline, which is polymerized with diamine diphenyl sulphone, the catalyst for this system is borontrifluoride. In reviewing literature from NASA's Ames Laboratory, and also in reviewing pyrolysis information from other Navy sources [a], the most prevalent compound to be found in a high temperature pyrolysis would be carbon dioxide. The NASA-Ames test conducted in conjunction with the Navy assumed a variety of "hangar scenarios", i.e., 2 aircraft and 15 aircraft, both low flame and high flame. Significant amounts of carbon monoxide were also present. The combination of these two resulted in an atmosphere that varied between 18 percent to 16 percent O_2. Carboxyhemoglobin levels in rats exposed to the smoke for 30 minutes approached lethal levels in the later case. Hydrogen sulfide was present at 100 ppm and in the high flame multiple craft scenarios hydrogen cyanide was also present at 100 ppm. I would expect all of these gases to have largely dissipated by the time these men were on the scene. Other potential sensitizers include the adhesive bonding which join the graphite epoxy with the aluminum or the

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[a] Reprint of 'Brief Review of Carbon Fiber Problem and the Potential Pulmonary Hazard' by Robert Hain in the Naval Aerospace Medical Institute's Reprints of Scientific Program from the 1980 Scientific Meeting.

aluminum alloy, and the graphite fibers themselves. These ordinarily would be tightly bound and therefore acutely, at least, totally inert.

Coincident with the above incident was the publication of 13 cases by Dr. Stewart Brooks (Brooks, 1985), who reported the existence of what he called the reactive airway dysfunction syndrome, RADS, which is an occupational asthma resulting from single exposure to an irritating substance. Although these two individuals gave no history of acute irritative effect, such a mechanism would be likely if a toxic substance were carried in on the graphite particles and later released in the bronchi and bronchioles, resulting in severe irritation. Chemists I have spoken with doubt the ability of crystalline carbon, graphite, to change in such a way as to be absorbent. However, the possibility that this mechanism was responsible was strongly emphasized in Executive Summary of the Workshop on Composites in Fires held in 1985[b].

My clinical assessment follows:

1) For Case 1: ventilatory studies and recovery are consistent with RADS. $(A\text{-}a)O_2$ gradient abnormalities on exercise testing do imply alveolar damage.

2) For Case 2: severity of symptoms not adequately supported by test of pulmonary function; however, $(A\text{-}a)O_2$ gradient abnormalities and improvement of FVC on PFT testing results do imply injury to both airway and alveoli.

Conclusions to be made from these cases are as follows:

1) Exposure to pyrolyzed graphite and other debris from F/A-18 aircraft may result in airway and alveolar injuries and in heightened airway reactivity in certain susceptible individuals.

2) The severity of alveolar damage for these affected individuals is impossible to assess. The role of adsorbed cadmium and H_2S in causing the diffusion abnormalities is somewhat feasible.

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[b] Workshop on Composite Fires 2-9 April 1985, Volume 1, Naval Post Graduate School 2-4 April 1985.

3) Inferring the conditions of this particular case on any other conceivable mishap is most difficult as this is a very unusual case. Despite the limitations of case reports in elucidating pathophysiology, it is apparent from the literature review and these cases that certain guidelines are best followed. These are: (1) For the "overhaul" stage of fire fighting/mishap investigation strict use of respirators with both dust and fume filtering capabilities. And, (2) for the fire-fighting phase of composite fire mishaps: use of Self Contained Breathing Apparatus (SCBA) is a necessity, and careful evaluation and observation of individuals with significant smoke exposure is warranted because of potential for presence of HCN, H_2S, and oxides of composite, the individual exposed to any or all of these may not manifest full effects for 24-72 hours.

ACKNOWLEDGEMENTS

Dr. Phil Harber, Chief Occupational Medicine Branch at UCLA provided clinical data in the Case 1 individual.

Dr. Alan Ducatmeen, currently Director of the Environmental Medical Science at MIT, provided literature data on prolysis products and generously acted as a sounding board in the assessment of these 2 Cases when he was Head of the Occupational Medicine Department at the Navy Environmental Health Center.

REFERENCES

1. American Lung Association/American Thoracic Society, Chronic Obstructive Pulmonary Disease 5th Ed., 1977.

2. Ballard, R., Gagliostro, M., et al, Chemical and Biological Analysis by Pyrolysis Atmosphere Generated by an Epoxy/Carbon Fiber Composite in NASA Technical Memorandum S-84274 for the Department of the Navy Naval Weapons Center, China Lake, CA.

3. Brooks, S., Weiss M., et al. Reactive Airway Dysfunction Syndrome (RADS). Persistent Asthma Syndrome After High Level Irritant Exposures, Chest 1985; 88:376-84.

4. Morgan, W., Seaton, A., Occupational Lung Diseases, 2nd ed., W. B. Saunders Company: Philadelphia 1984.

5. Parker, R. W., Occupational Lung Disorders, 2nd Ed., Butterworths: London 1982.

IMMUNE DYSFUNCTION IN CHEMICALLY INDUCED ILLNESS: A PROBLEM FOR CERTAIN COMPOSITE WORKERS?

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ABSTRACT

Certain chemicals have long been known to produce allergic disorders of the skin and lung in laboratory animals and in human beings.

The growth of immunology as a rigorous experimental discipline within the biological sciences has provided interested communities with startling concepts and a rich, though esoteric, vocabulary. A climate for misinterpretation of tests and application of pseudoscience exists. The classic types of serum and cellular hypersensitivity described over many decades of this and the last century are postulates that still must be satisfied when new hypotheses are evaluated.

One molecule of small molecular weight, formaldehyde, present in some composites, does raise immune responses in the skin, through the Type IV cellular hypersensitivity mechanism. It has been postulated that formaldehyde raises serum antibodies that are indicative of exposure, and, further, represent objective evidence of chronic polysymptomatic illness involving several organ systems, including the digestive tract and the nervous system. Current professional experience, as indicated by the medical literature, does not support these findings or conclusions. Also, convincing dose-response relationships have not been found.

The presence of chemical odor, particularly if acrid or nauseating, could be disquieting. Attention to odor ventilation, microenvironments, protective equipment and worker attitudes is important.

Workers who have been told they have life threatening illnesses due to workplace exposure may show anger, fear and hostility appropriate to their belief. This distrust may not yield until enough science has been applied, generally known, and accepted.

PRESENTATION

Certain chemicals have long been known to produce allergic disorders of the skin and lung in laboratory animals and human beings.

I will speak of three chemicals of low molecular weight currently associated with skin and respiratory illnesses in composite workers: toluene diisocyanante (TDI), trimellitic anhydride (TMA) and formaldehyde (F).

The American College of Physicians has an excellent educational offering, the Medical Knowledge Self Assessment Program (MKSAP VIII) (1988-9). The first question in the booklet on General Internal Medicine deals with chemically-induced occupational asthma (Chan-Yeung, 1986). About five percent of persons who work with TDI or its related compounds will develop hypersensitivity-type respiratory problems. The case reported concerns a 23-year-old male who installs polyurethane insulation at a boatyard. He presented at the emergency room eight hours after his shift with wheezing and coughing. There was no prior history of asthma or atopy.

One of the questions raised was whether the worker should be removed from his job. The answer was that the employee should be removed from the exposure by substitution of other materials, not the job. This case is presented because it typifies a health effect of chemical exposure common today. Health care workers in the composite field should be acquainted with immune mechanisms that underlie skin and lung disorders associated with chemical exposure.

There are four types of immune hypersensitivity. These are shown in Table 1, which is adapted from a textbook (Gell et. al, 1975) on clinical aspects of immunology. The information in the table looks at aspects of immune function such as antigen, antibody, cell types, and complement and latency. "Complement" is the name for a complex and aggressive enzyme system that drills holes in cell walls.

Type I hypersensitivity, pertinent to our discussion, produces classic symptoms of asthma. It involves the production of IgE class antibodies against various antigens, e.g., pollen. Complement is not involved. However, fixed tissue mast cells secrete histamine and induce other aspects of the inflammatory response, and reactions can be severe.

TABLE 1

TYPES OF HYPERSENSITIVITY

Type	Antigen	Antibody	Complement	Cells	Latency	Example
I	Allergen	IgE	O	Mast	Imm.	Hay Fever Asthma
II	On Cell Surface	IgG	+	K	Imm.	Transfusion Reaction
III	Protein	IgG Immune Complex	+	Polys + Tissue	Hours	Farmer's Lung
IV	Toxin or Hapten	None	0	T	Days	Poison Ivy

Recently it has been shown that chemicals of low molecular weight such as trimellitic anhydride (TMA) can combine with human serum albumin (HAS) to form a stable complex (TMA-HAS). Such a complex has been called a "new antigenic determinant" (NAD) by Patterson and co-workers (1981). High titers of IgE antibodies are raised in animals and human beings. Passive transfer has been demonstrated. Thus the chemical trimellitic anhydride (TMA) can act as a hapten to modify human serum albumin, raise antibodies, produce a defined and recognized illness (TMA "flu"), be accurately diagnosed by clinical and laboratory methods, and be demonstrated in the animal model. The tenets of Type I hypersensitivity are satisfied.

It has been postulated by Broughton and Thrasher (1988), using the methods described by Patterson et al., that gaseous formaldehyde (F) may cause a spectrum of symptoms and illness in persons exposed in new buildings and at work. They have published data purporting to show significant antibody titers against F-HAS in such subjects. Further, in the case of formaldehyde, the illness hypothesis has been broadened to include other immune dysfunctions such as altered T-cell ratios, increases in T-cells bearing surface

markers to Interleukin-2 and Tal, increase in antibodies to smooth muscle and parietal cells, and an increase in mitogenesis and blastogenesis.

Although it is known that formaldehyde is an irritant, and a skin sensitizer by the Type IV hypersensitivity mechanism (Table 1), it is not clear that formaldehyde is a Type I lung sensitizer, or that it produces chronic debilitating illnesses of the type suggested by Broughton and Thrasher. In fact, the bulk of medical evidence is against this hypothesis. However, it is true that no adequate population study has been done to settle this interesting and important question, whether formaldehyde raises antibodies that can be correlated with a definite illness.

Patterson et al. (1987) have recently written in the Journal of Allergy and Clinical Immunology that "it has not been proved that inhaled F results in F-self-protein complexes that produce IgE antibody-medicated reactions or IgG mediated immune complex damage. At this time the burden of proof rests on those who propose such mechanisms."

The growth of immunology as a rigorous experimental discipline within the biological sciences has provided interested communities with startline concepts and a rich, though esoteric, vocabulary. A climate for the performance and misinterpretation of tests and the application of pseudoscience exists.

Workers who have been told they have life-threatening illnesses due to workplace exposure may show anger, fear and hostility appropriate to their belief. This distrust may not yield until a measured amount of scientific study has been applied, generally known, and accepted.

REFERENCES

BROUGHTON, A., AND THRASHER, J. (1988). Antibodies and Altered Cell Mediated Immunity in Formaldehyde Exposed Humans, in Comments Toxicology 2: 155.

CHAN-YEUNG, M. LAM S. (1986). Occupational Asthma. Am. Rev. Resp. Dis. 133: 686-703.

GELL, COOMBS, AND LACHMAN (1975). Clinical Aspects of Immunology, 3rd Ed., Chapter 25, pub. Blackwell.

PATTERSON, R., ET AL. (1981). Characterization of Hapten-Human Serum Albumins and their Complexes with Specific Human Antisera. J. Allergy Clin. Immunol. 1: 181.

PATTERSON ET AL. (1987). Formaldehyde Reactions and the Burden of Proof. J. Allergy and Clin. Immunol. 79: 705.

OCCUPATIONAL HEALTH ASPECTS OF ADVANCED COMPOSITE MANUFACTURE AND USE

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ABSTRACT

3M describes its occupational health experiences during 35 years of composite manufacture and customer applications. The results of several studies conducted by 3M Laboratories on the Scotchply™ products are shared. Recommendations are made on research that would help industry better understand the health hazards of advanced composites.

In only five instances were adverse health effects reportedly associated with Scotchply™ composite manufacture. There were two reports of vapor overexposures attributed to hardeners no longer used in manufacture, one case of dermatitis and two cases of allergic skin reactions seemingly attributed to multifunctional epoxy resins. 3M has a medical policy of precluding personnel with histories of skin disorders and allergies from working in epoxy handling operations such as composite manufacture. There is no specialized medical surveillance program for composite personnel since standard exposure control techniques can successfully minimize exposures to epoxy resins, curatives, and fibrous reinforcements. Minimizing worker exposures to vapors and gases during coater clean-up and resin exotherms are the primary industrial hygiene concerns.

3M is not aware of specific customer health problems attributed to composites but commonly receives questions about precautions to take during handling. Customers are encouraged to avoid eye and skin contact with prepregs and properly vent material during curing and processing.

INTRODUCTION

3M is a diversified company with over 81,000 employees worldwide and over 10 billion dollars in annual sales. The corporation provides more than 50,000 products to a wide variety of markets including the commercial, consumer, and industrial sectors. There are

more than fifteen 3M divisions providing products to the aerospace and defense-related markets.

For more than thirty-five years, 3M has been researching, developing and manufacturing advanced composite materials commonly known in the aerospace industry by the Scotchply trademark. As a member of the Suppliers of Advanced Composite Materials Association (SACMA) and as a company with a staff of 32 toxicologists, industrial hygienists and physicians, 3M welcomes the opportunity to share occupational health knowledge.

Scotchply™ composites are structural grade, fiber-reinforced resin matrix materials. The products are supplied to customers as prepregs and as cured sheets ready for fabrication into finished parts. Most of the Scotchply™ products are unidirectionally aligned and composed of epoxy resin impregnated continuous glass filaments. For prepregs, the fibers are impregnated with one or more epoxy resins and sold as uncured rolls containing a controlled ratio of reinforcement to resin. The filaments are aligned in parallel and non-woven (i.e., without cross-overs within a ply) to minimize abrasion under stress. The individual plies can be cross-oriented at almost any angle to meet customer design specifications. 3M offers related groups of Scotchply™ products using aramid, carbon, and "S" glass fibers as reinforcements.

During our thirty-five year experience, 3M has had very few problems related to customer and employee exposures to composites. Customer files, occupational health records and discussions with laboratory and manufacturing personnel having long-standing affiliations with the Scotchply™ product line were used to trace our history. Although we commonly receive customer questions about the proper handling and curing steps to follow, we are not aware of specific customer health problems. In our research and manufacturing sites, we are aware of only five reports of health effects attributed to raw materials used in composites. There is no special medical surveillance program in place for composite workers since engineering controls, personal protective equipment and employee training can be used successfully to minimize exposures to the epoxies, hardeners and fibrous reinforcements.

PREPREG TOXICITY OVERVIEW

3M's knowledge of material toxicity combined with an exposure control program probably explains why there are so few complaints. A brief overview of the health effects of the raw materials used in 3M's composites provides background for our industrial hygiene program and the recommendations made in the Material Safety Data Sheets (MSDSs) for the Scotchply™ products.

Epoxies

Most of the epoxy resins used in composite manufacture are based on the reaction of bisphenol A and epichlorohydrin. Residual epichlorohydrin, an animal carcinogen (IARC Monographs, 1976), is usually present at less than one part per million by weight in the epoxies. Direct contact with mixtures or solutions of these resins may result in serious irritation of the skin and eyes. Bisphenol A resins can be skin sensitizers producing allergic reactions in certain individuals. Solvents may enhance these skin sensitizations.

Many of our formulations use mixtures of monofunctional and multifunctional epoxies. People handling these raw materials and customers handling the uncured composites should understand that multifunctional epoxies are more irritating and sensitizing than monofunctional epoxies. There were two cases of skin allergies in the Scotchply™ manufacturing site associated with the use of multifunctional epoxies.

Amide Hardeners

Amide hardeners such as dicyandiamide seem to be only slightly irritating. Cases of skin sensitization have not been reported. Systemic effects have not been noted Airborne particles are considered nuisance dust although neither a Threshold Limit Value (TLV®) nor Permissible Exposure Limit (PEL) has been established.

Aromatic Amine Hardeners

Aromatic amines are considered to be only slightly irritating to the skin. There is a concern that this class of compounds may cause systemic toxicity, especially liver effects (IARC Monographs, 1985). With the exception of methylene dianiline, little is known about the skin permeability of aromatic amine hardeners. As a result, inhalation and dermal exposure should be avoided.

N'-(4-Chlorophenyl)-N,N-dimethylurea (150-68-5)

Monuron, which is a N'-(4-chlorophenyl)-N,N-dimethylurea, is considered an animal carcinogen by the International Agency for Research on Cancer (IARC) (IARC Monograph, 1985). The urea compound was tested in both rats and mice by oral administration. In one study, an increased incidence of lung tumors was observed in male mice. In another study, tumors were observed in male rats in an 18-month daily feeding study. To date, monuron has not been found to cause cancer in humans.

Bis(4-aminophenyl)sulfone (80-08-0)

Bis (4-aminophenyl)sulfone, commonly known as DDS or dapsone, is a moderately toxic chemical based on a number of animal studies (SACMA, 1988). Because of its pharmaceutical applications, much is known about human exposure to DDS. At doses that would be very difficult to mimic in industrial settings, DDS is known to cause blood disorders (IARC Monographs, 1980). The National Cancer Institute (NCI) found that oral administration of DDS caused tumors of the spleen in male rats and tumors of the peritoneum in two animal studies. In addition, an increase of tumors of the thyroid was found in rats of both sexes in one study and in males in another study (IARC Monographs, 1980).

Chronic oral administration of DDS to humans during pharmaceutical studies does not provide evidence of human carcinogenicity (IARC Monographs, 1987a). NCI has speculated that the different responses between man and rodents are probably due to increased metabolism (i.e., detoxification of the compound in man as compared to rats) (SACMA, 1988).

Methylene dianiline (cas. no. 101-77-9)

3M avoids the use of methylene dianiline, MDA, in our composites because of its known potential to cause chronic effects, especially liver toxicity, and because of IARC's carcinogenicity rating of 2B (IARC Monographs, 1987b).

3-(3,4-Dichlorophenyl)-1,1-dimethylurea (330-54-1)

3-(3,4-Dichlorophenyl)-1,1-dimethylurea is commonly known as diuron. It is a mild eye and skin irritant, appears not to be a skin sensitizer and is slightly toxic by the oral and dermal routes of exposure (Haskell Laboratories, 1983). Diuron appears to cause very

limited chronic toxicity in the rat, mouse and dog. Moreover, it did not demonstrate any oncogenic activity in any of these three species. Diuron does not appear to be teratogenic or mutagenic (Haskell Laboratories, 1983).

N,N'-(Methyl-1,3-phenylene) bis(N,N'-dimethylurea) (26604-41-1)

TDI/urea or N,N'-(Methyl-1,3-phenylene) bis(N,N'-dimethylurea) is considered an eye and skin irritant. No other toxicity information is known at this time.

Aromatic amines as a class of compounds are currently being highly scrutinized by the Environmental Protection Agency (EPA). The agency is building a data base of toxicity testing for this group of compounds. In all likelihood, any new aromatic amines that are submitted to EPA under the Premanufacturing Notice (PMN) process will be compared structurally to MDA. Therefore, any new aromatic amine may be suspected of causing carcinogenicity, retinopathy, hepatotoxicity and reproductive toxicity. As you can well imagine, the investment in developing toxicity test data for new aromatic amines is going to be significant.

Fibers/Reinforcements

Most of the reinforcing materials used in the industry have the potential to cause eye, skin, and upper respiratory tract irritation as a result of the mechanical irritant properties of the fibers. A current concern is whether or not these fibers cause chronic lung disease, including cancer. 3M believes that the fibers used in Scotchply™ composites are too large in diameter to penetrate into the lungs and cause chronic lung disease. Although 3M has not monitored workplace exposures, we are confident that airborne concentrations of these materials do not approach the exposure limits outlined in Table 1.

Another concern is that there may be synergism between the mechanical irritation caused by the fibers and the chemical irritation caused by the composite resins. This is another reason to avoid skin contact with composites.

MEDICAL SURVEILLANCE

3M does have a policy of excluding employees with a history of skin disorders from work in epoxy-handling operations including Scotchply™ manufacturing. New employees complete pre-employment health screening questionnaires in which they are asked about

TABLE 1

RECOMMENDED/REQUIRED EXPOSURE LIMITS FOR FIBERS USED IN SCOTCHPLY™ MANUFACTURE

FIBERS	EXPOSURE LIMITS TLV (R)	PEL	MANUFACTURERS' RECOMMENDATIONS
GLASS	10 mg/m^3		
CARBON (SYNTHETIC)	10 mg/m^3*		
ARAMID			5 respirable fibrils/cc
CERAMIC			2 fibers/cc**

* < 1 percent quartz
** 3M Exposure Guideline, fibers < 5 micron diameter

skin disorders. Workers developing any skin problems are given medical restrictions prohibiting them from working in epoxy-handling areas. 3M has not established a special medical surveillance program for its composite personnel. The Medical Department does not believe that a special program is warranted based on information available at this time. The exposure potential of a Scotchply™ worker is believed to be low for all steps of the manufacturing process. 3M's emphasis has always been to minimize exposures through engineering controls, employee training, and personal protective equipment. Based on information available at this time, we believe that if workplace exposures via the respiratory tract and skin are properly controlled, special medical surveillance programs are not needed

INDUSTRIAL HYGIENE OVERVIEW OF MANUFACTURING

Composites are coated at a manufacturing facility in St. Paul and converted at another site a short distance away. Rovings of fibers are fed into a coater where they are saturated with epoxy resin blends. The resulting web is laminated to a paper backing and wound onto a large roll. Industrial hygiene concerns and exposure controls at various points of this process are described.

Hardeners such as functional amines are transferred from drums into an automated charge system with the operator positioned in a remote location. In a special containment room, the hardeners are metered out to a mix tank. During periodic cleaning of the room,

operators wear coveralls, gloves, eye protection and a dust/mist respirator. Employees, through hazard communication training, have been informed of the potential hazards of overexposure to these materials and the proper precautions to take.

Epoxy resins are charged from bags into mix tanks with the use of local exhaust ventilation. Operators wear coveralls and gloves during the brief charging step. Time-weighted average exposures to epoxy resin dust have been measured at less than 1 mg/m^3 which is considered quite low even though recommended exposure limits have not been established.

Epoxy resins and curatives are fed to the coater at elevated temperatures. Local exhaust ventilation is provided above the coater for vapor control. General room ventilation is sufficient in the area of the coated web and wind-up station.

Rovings of fibers are fed into the coater. Coveralls with long sleeves and gloves are recommended to minimize fiber exposure. Limited air monitoring data indicate that airborne fiber exposures are low. The glass fibers of 10-12 micron diameter are classified as nuisance dust.

We are aware in only five instances during the 35 years of Scotchply™ manufacture of adverse health effects reported by workers. In 1988, one dermatitis case was reported among approximately 40 employees involved in Scotchply™ manufacture. It is not known if the epoxies, fibers or the mixture was the cause of his reaction. The other four reports of health problems are somewhat sketchy. Over the years, two employees reported skin allergies noticeable when multifunctional resins were being used. These workers were removed from the operation. In another instance, methylene diamine was used as a hardener. Two employees reported that the hot vapors from the coater were extremely irritating. Use of the material was discontinued.

Employee training programs dealing with the potential skin hazards of handling fibers, epoxy resins and hardeners have been in place for several years. Appropriate use of skin protection, barrier creams and good personal hygiene practices have been emphasized

Two of the main industrial hygiene concerns of composite manufacture are clean-up and epoxy exotherms.

The solvent, trichloroethylene, is used to clean the coater station. The short-term exposures of operators to vapors have been monitored and found to be slightly excessive during a 10-15 minute clean-up. As a result, entry to the coater room is limited to authorized

personnel. Employees wear organic vapor respirators and skin and eye protection during the clean-up. Signs controlling entry are posted on access doors.

On occasion, epoxy resin exotherms occur at the coater head. The hot resin is immediately placed in a 55-gallon drum partially filled with water. The drum is then placed in a well ventilated enclosure for control of released gases, vapors, and smoke. The epoxy material is completely covered with water and allowed to cool. Disposal is according to 3M's recommended practices and local regulations. Building security is notified to respond to questions about any exotherm odor.

Uncured jumbo rolls of composites are shipped to another building for converting. The rolls are laminated into different thicknesses and different angles depending upon customer specifications. The composites are then prepared for final layup.

Overall there have been very few industrial hygiene problems in composite manufacturing. As mentioned earlier, we are aware of only five reports of ill effects which could have been prevented if appropriate exposure control measures were followed. We believe that the use of engineering controls, personal protective equipment and employee education and training can successfully minimize occupational health problems.

CUSTOMER OVERVIEW

3M is not aware of any customer health problems related to the Scotchply™ products. Based on our knowledge of the materials and our general knowledge of customer applications, the following concerns and safeguards are emphasized in our product Material Safety Data Sheets.

Concerns

1) Direct eye contact with uncured prepreg may cause irritation. Dust created during the processing of cured material may also cause eye irritation.

2) Repeated or prolonged skin contact with uncured epoxy prepreg may cause irritation. Allergic skin reactions may occur in certain individuals.

3) Vapor of heated material and dusts created during final processing may irritate the respiratory system.

Precautions

The precautions recommended on the product MSDSs include:

1) Avoid contact with eyes and skin when handling uncured product. Wear eye protection and impervious gloves when handling uncured product.

2) Wash hands thoroughly after handling uncured product. Remove contaminated clothing and launder before reuse.

3) Avoid breathing vapors released during curing operations. Properly vent curing ovens to the atmosphere or to a suitable emission control device. Do not recirculate emissions into the workroom air. Avoid inadvertent recirculation of air exhausted on rooftops through make-up units by proper positioning of exhaust stacks and intake units.

4) Avoid breathing dust emitted during cutting, grinding, or sanding of the cured product. Use water as a lubricant on machining tools to eliminate dust. Wear appropriate eye protection. If adequate local exhaust ventilation is not available, wear an approved dust respirator such as the 3M 8710.

COMPOSITE ANALYSES

Several studies have been conducted at 3M Laboratories on finished Scotchply™ products both in the cured and uncured forms. A brief summary of the findings follows.

1) Dust from cured and machined Scotchply™ prepregs was analyzed at our Central Research Laboratory. Decomposition products of epoxy resins and a component which appeared to be dioctyl phthalate were found.

2) A sample of Scotchply™ resin blend containing epoxy resin and dicyandiamide was heated to 300°F for five minutes to initiate an exotherm. The major components identified using mass spectroscopy methods included carbon dioxide, methyl ethyl ketone, and methyl chloride. Quantification of components was not conducted.

3) Small quantities of monuron vapor were released during heat curing (220°F-260°F) of several Scotchply™ products. The toxicological data available at this time is inadequate for establishing an exposure guideline for airborne monuron. Human exposure to monuron vapor is expected to be negligible under the recommended conditions of curing in an oven vented to the outdoors.

4) Research at 3M indicates that monuron can be leached from uncured prepregs. For example, 0.6-1.3 milligrams of monuron per gram of prepreg were leached into water (pH=7 at room temperature) in 15 hours. In water with a pH of 4.4 at room temperature, 5.6 milligrams of monuron per gram of prepreg was leached in a 24-hour period. Employees handling prepregs containing monuron should be trained and required to wear gloves and other protective equipment, wash after handling, and keep food, drinks, and tobacco products out of the work area.

SUMMARY AND RECOMMENDATIONS

What does 3M know about the health effects of epoxy based composites? Our experience indicates only minor occupational health problems associated with the manufacturing of Scotchply™ products. We are not aware of any customer health-related problems. Exposures can be successfully controlled during manufacture by good engineering design, personal protective equipment, and employee training. We believe that customer problems can be avoided by following the precautionary information provided on MSDSs.

What don't we know? Certain manufacturing exposures such as charging of hardeners and fiber handling have not been measured. Although we are confident that the exposures are well within recommended guidelines, exposure measurements will be taken in the near future.

3M does not have any exposure data from customer operations in which either cured or uncured Scotchply™ products are being used. This type of information, which can vary from operation to operation, would be very helpful to the conference.

What do we need to know? At this time, 3M does not believe a special medical surveillance program is necessary for composite workers. However, we are open to change if new information obtained during this conference indicates that a special program is in order.

Curing oven emission air sampling studies should be continued to further identify contaminants. While this would be valuable information, venting ovens to outdoors as recommended in our MSDSs should prevent any health problems.

REFERENCES

Haskell Laboratories, "Technical Data Sheet for Diuron," 1983.

IARC Monographs, Volume 11, p. 131. 1976.

IARC Monographs, Volume 39, pp. 347-365, 1985.

IARC Monographs, Volume 24, p. 59. 1980

IARC Monographs, Supplement 7, p. 185, 1987a.

IARC Monographs, Supplement 7, p. 66, 1987b.

Suppliers of Advanced Composite Materials Association (SACMA), "Safe Handling of Advanced Composite Materials Components: Health Information," Draft H, pp. 20-21, November 1988.

4,4' - METHYLENEDIANILINE: INDUSTRIAL HYGIENE EXPERIENCES

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ABSTRACT

Within the last 14 months, numerous industrial hygiene field evaluations of 4,4' - methylenedianiline (MDA) were conducted which included about 33 air samples and 69 wipe samples. This presentation highlights the findings of seven industrial processes, discusses emergency response/clean up, and presents some of the issues surrounding MDA that may trouble the industrial hygienist Cutting, trimming and lay up by hand can produce measurable airborne MDA. Ventilation controls for cutting and trimming are not straightforward, since continuous air movement can dry out the product in some cases and create a far worse dust problem Ventilated hand tools and back draft benches are suggested as options. Air spraying MDA-containing material in a large, well ventilated spray booth can apparently result in breathing zone concentrations in the neighborhood of 5 ppb, the proposed OSHA "Action Level". In order to adequately protect a spray painter from dermal absorption of MDA, inhalation of isocyanates, and heat stress, a substantial but workable complement of personal protective gear is required. A filament winding machine can present many obstacles to proper ventilation controls, but it has been accomplished with good results. An overhead plenum with an air curtain on each side and exhaust plenums at the floor which also serve as walking surfaces are two of the distinctive features of the ventilation controls implemented. A dust enclosure with HEPA filtered exhaust for spools and rollers is another essential feature for prepreg winding. Breathing zone air samples for MDA at a well controlled filament winder have ranged from "none detected" to 0.6 ppb. Cleaning the dust enclosure presents the highest exposure potential.

Wipe sampling can be of significant value as part of the hazard evaluation, though no scientific protocol for their collection or interpretation exists as yet. This presentation also outlines some proper actions to take if an uncontrolled release of MDA-containing dust occurs, including medical evaluation of the cohort with the highest risk. Ten micrograms per 100 cm^2 is presented as a possible target for "clearance" wipe samples. Finally, attention is called to some problems related to MDA hazard evaluation and control, such as "regulated

areas", metamorphoses of the hazard from tacky to dusty and from uncured to cured, wipe sampling, waste disposal, and selection of personal protective gear.

INTRODUCTION

The purpose of this presentation is to share my industrial hygiene experiences with 4,4' - methylenedianiline (MDA), particularly field evaluation and engineering controls. If there is anything unique about my MDA experiences, it would probably be 1) the emphasis on the filament winding process, 2) extensive wipe sampling, and 3) emergency response and clean up.

As an overview, within the last 14 months approximately ten separate field evaluations were conducted which involved some form of sampling. The samples total about 33 air samples, 69 wipe samples, and one bulk material analysis. Additionally, a number of field evaluations involved no sampling.

This discussion will be organized by manufacturing processes, roughly in order of ascending industrial hygiene complexity, with comments on industrial hygiene samples, if any, engineering controls, and personal protective devices. I will conclude with some commentary on emergency response and special problems.

DISCUSSION

The first process, compression molding, presents few special problems. A canopy hood drawing about 150 feet per minute past the unobstructed cross section of the face can be installed over the hot press. The canopy may need to accommodate electrical and high pressure lines in the back, and even the blow down tank. Scrolling sides are ideal for allowing easy maintenance access. Personal protective gear is not a critical issue here and may be no more than industrial safety glasses and thermal gloves.

Ovens and autoclaves which are not otherwise exhausted or purged may require a flanged canopy over the door. Vacuum lines from autoclaves must have a liquid trap or a cold trap and exhaust to the outdoors. These lines must be flushed to keep them from clogging and requiring frequent maintenance. Gas fired autoclaves can recycle the vacuum line waste to the burner. Special personal protective gear should not be required under normal operating conditions.

Resin transfer molding presents a possibility of splattering resin in some cases if pressurized lines can pop loose from a connection. A controlled access area is advisable, as well as chemical splash goggles, disposable lab coats, and gloves selected for the solvents present in the resin system. Preparation and clear up of the pressure pot and other equipment should be done under a ventilated hood. Since clean up may involve a solvent requiring a different glove, a combination of the two should be worn, if possible, with the cleaning solvent protective glove on the outside. If this operation is set up as a "regulated area", but loses its status as such when the job is done, wipe samples should be collected after clean up is completed.

Tube braiding operations where an MDA-containing curing agent is initially heated to 150°F or so, mixed with the base resin, and rubbed onto tubes is not expected to present detectable airborne amounts of MDA (Fig. 1). However, I have observed low levels of meta-phenylenediamine (MPDA). This task tends to present some dermal contact potential. All potentially contaminated surfaces, especially the floor around the braider and the drying rack, should be covered. Personal protective gear should include disposable coveralls, chemical resistant gloves, shoe covers, and industrial safety glasses. Careful consideration should be given to glove selection since glove contact can very nearly simulate glove immersion. Gloves should be changed almost hourly, depending on the length of the task, employee work practices, effectiveness of the glove, and temperature of the resin. Organic vapor air purifying respirators should be available but are not likely to be necessary with good general ventilation. Mixing and weighing the chemicals should be performed under a ventilated hood. Braiding machines, in my experience, seem to be equipped for hookup to ventilation which would control fiber release from the rotating spools at the periphery of the circle, but not vapors released near the center of the machine. As with resin transfer molding, wipe samples should be collected at the end of the job if the "regulated area" status is eliminated.

The next process we will touch on is cutting, trimming, and lay up by hand (Fig. 2). MDA-containing prepreg was observed to yield detectable levels of MDA in employee breathing zones where the prepreg remained tacky, there was no local exhaust ventilation, and the temperature of the material during lay up was kept below 150°F. The higher results were seen at the cutting and trimming task. The hand tool used to cut can make a significant difference judging from visible emissions. A very sharp straight blade seemed to

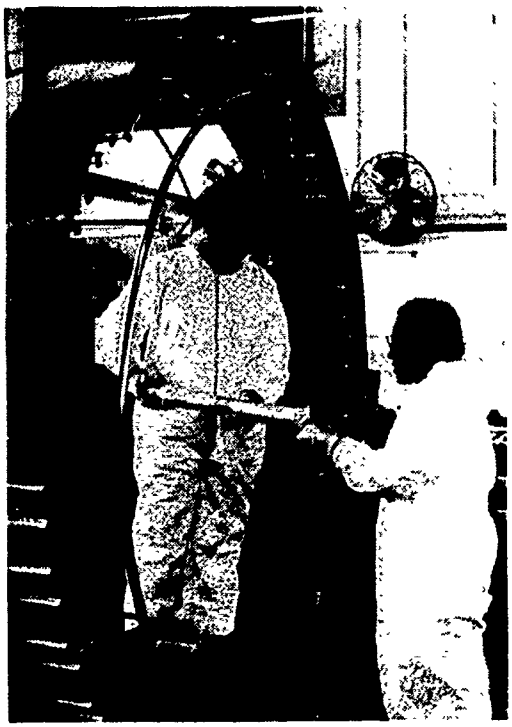

Figure 1. Tube braiding operations.

Figure 2. Hand lay up with composites.

be better than a rotating blade or "pizza cutter" type hand tool. Stripping and peeling by hand is worse yet, and should be discouraged. Some form of ventilation would seem prudent, but air passing over the plies dries it out faster and creates a potentially more significant dust exposure. A HEPA filtered ventilated hand tool may be the best alternative. If the quality and engineering components of the organization will approve light solvent wiping to maintain tackiness, and the parts are not too oversized, a backdraft hood may be the best option. Protective gear should include a disposable lab smock, shoe covers to minimize spread of contamination, and specially selected chemical protective gloves, which should be disposed of at least at the end of the shift.

Another process, possibly the most important in terms of potential exposure, is spray coating with MDA-containing systems. Dispensing and weighing small amounts of MDA-containing curing agent has yielded measurable amounts of MDA in the worker breathing zone. Spray coating in a large, well ventilated spray booth has been observed to result in breathing zone levels of MDA in the neighborhood of 5 ppb, the proposed action level for MDA. This apparently means that the special "Action Limit" requirements of the OSHA Advisory Committee's proposed rule on MDA might apply to conventional manual air-assisted spray application of MDA-containing materials. In this case, possibly the most notable requirement under the proposed OSHA standard would be that employers ensure that the exposed personnel shower at the end of the work shift. Personal protective gear for spray applications should be sufficient to ensure a reasonable level of protection from skin absorption and inhalation of isocyanates which may also be present. Better skin protection probably means non-breathable coveralls, which in turn means potential heat stress. Often environmental requirements for the sprayed material make it necessary to heat the spray booth supply air up to 80°F or greater, exacerbating the heat stress problem. One option for reasonable protection would be a chemical protective non-breathable disposable coverall, a hood type supplied air respirator with a cooling vortex and long shroud tucked into the coverall to help cool air reach the torso of the worker, shoe covers, and a carefully selected chemical protective glove, usually aimed at protection from the solvent diluent in the sprayed material, and a latex surgical glove or cotton liner underneath to help in doffing the protective gear without contaminating the hands.

A process which can involve a complex ventilation control strategy is filament winding. An R&D filament winder, which is capable of winding 3- to 20-foot parts with a wide variety of

types of filaments and resins, prepregs, and various heating and imidizing capabilities would seem to defy ventilation controls (Fig. 3). Ventilation considerations include some means of local exhaust for a resin bath for wet winding, a dust enclosure for prepreg winding, and ventilating a 20-foot mandrel which must accommodate 1) hoisting parts in and out of place, 2) a generous sphere of hands-on accessibility, and 3) a 30-inch tall winding head with multiple axes of movement. The seemingly impossible has been accomplished, although it be imperfect, and with very satisfactory results to date. First, a small local exhaust canopy with about 15 feet of flexible duct can control resin bath vapors while wet winding. For winding prepreg, the canopy is replaced by a medium size two-chamber Plexiglas® dust enclosure with a HEPA filter in line. This encloses the spools, rollers, solvent brushes, and eyelets, and stays under negative pressure with very little air movement. Large quantities of passing air would quickly dry out the spools of raw material. The mandrel has suspended over it a plenum which is divided into two chambers down the length of the mandrel, and receives forced air at both ends of each chamber (Fig. 4). Two slots running the length of the mandrel on the bottom edges of the plenum provide a strong air curtain which helps to separate the workers from the vapors issuing from a large part which could be very hot. Air is exhausted near the floor from two narrow plenums which also run the entire length of the mandrel. One is on each side of the mandrel. These act as receivers for the air curtains, and exhaust more air than is supplied, as is recommended for all push/pull ventilation systems. This also helps to maintain negative pressure in the room. They are covered with perforated metal and provide a partial work platform for employees standing near the mandrel and involved in the work. Air samples for MDA have ranged from undetectable to 0.6 ppb. Exposure potential is highest during the cleaning of the dust enclosure. Minimum protective gear during filament winding would be comprised of disposable coveralls, shoe covers, chemical protective gloves with cotton liners, and industrial safety glasses. During the cleaning of the dust enclosure, additional protection may be required, such as a half-face air purifying respirator and a head covering while using a HEPA vacuum and wiping with water. The floor and all working surfaces subject to dripping resin should be covered with disposable protective coverings. Wipe sampling is important for clearance if the area is to be used for less hazardous materials and personnel will re-enter the area without protective

Figure 3. Filament winding machine with push/pull ventilation system.

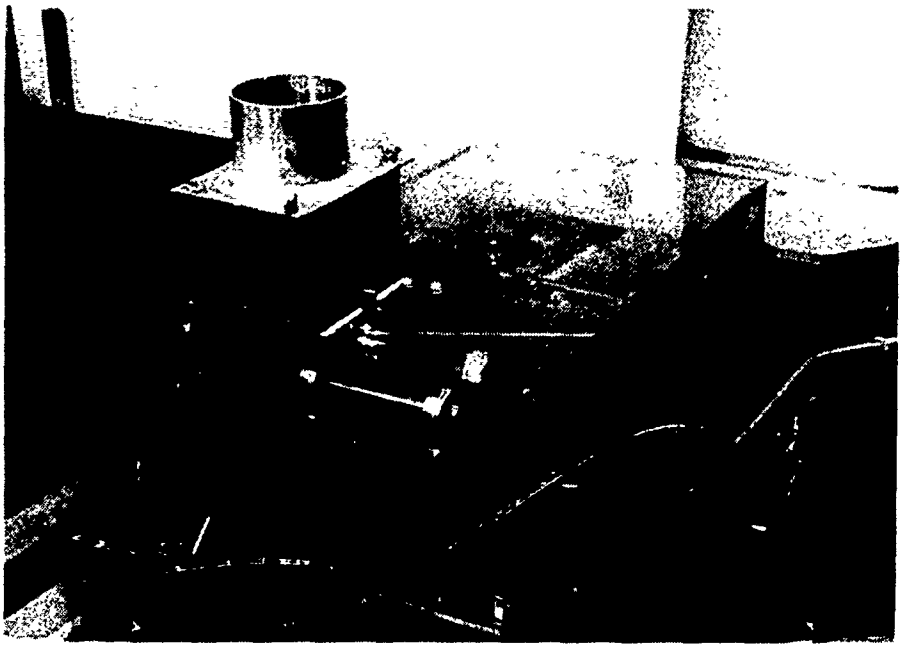

Figure 4. Two-chamber Plexiglas® dust enclosure with HEPA filter.

apparel. However, there is as yet no scientific protocol for collection of wipe samples for MDA or the interpretation of wipe sample results. Using 10 micrograms per 100 cm^2 has proved to be a useful target clearance level based on a number of assumptions including an estimate of skin contact area per day and 2 percent skin absorption. Thorough decontamination of the area is required before personnel are allowed back in the area without protective attire.

In processes involving prepreg, it is critical to maintain a tacky consistency of the material, otherwise, in drying out, a severe dust hazard may be encountered. Brittle imidized material also must not be disturbed in any way that produces a particulate hazard If a large amount of MDA-containing dust is generated in an uncontrolled process and is either visible in the air or has grossly contaminated horizontal surfaces, the area should, of course, be evacuated immediately. Ventilation must be shut off and access to the area must be sealed The extent of contamination can then be more accurately assessed visually and by air and wipe samples. The investigator must be careful to wear appropriate protective gear. If necessary, a decontamination structure can be set up similar to an asbestos abatement job with air locks and negative pressure ventilation. A minimum of two decontamination passes should be made, once with a HEPA vacuum and then a wet wipe. Aggressive air clearance samples and wipe clearance samples are critical. A timely investigation must be conducted to determine the personnel who entered the room during the uncontrolled release of material and how long each person spent in the area. They can then be grouped into risk categories, or cohorts. At this point an industrial hygienist must work closely with medical personnel. He may need to use limited available data to make a recommendation to the physician as to which risk group or groups should get prompt medical evaluation. The degree of actual need for medical evaluation must be balanced with caution against causing employees undue alarm. The OSHA-proposed rule addresses emergency examinations, indicating that it should include a brief history, appropriate physical examinations for signs relating to the liver and skin, a liver function test and any other tests deemed appropriate by the physician. If any abnormalities are noted, the next higher risk group or groups may receive similar treatment, and so forth. However, certain aspects of the medical evaluations may not be an adequate gauge of exposure beyond about a week after the incident.

Finally, I will touch on a few of the weightier unresolved issues that may trouble the industrial hygienist whose charge is to ensure the well being of employees who must work with MDA-containing composites. There is always the tension of deciding how far to go in implementing the requirements of a rule that is not made law yet. The mediated Rulemaking Advisory Committee made their recommendations for MDA in July of 1987, but the certainty of law in the form of a final rule is slow in coming. This also contains the question of "regulated areas". Defining regulated areas forces hard choices on segregation and dedication of equipment, deciding the scope of a medical surveillance program, and the worthiness of total decontamination after each MDA use. Furthermore, regarding decontamination, how clean is clean enough? What criteria is to be used for clearance? There is the problem of build up of contamination so that clearance becomes harder to achieve. Another puzzling issue is the changing nature of prepreg as it dries out. When is it too dusty to be safely worked with? And in the same vein, how cured is cured enough if the process calls for grinding or sanding a coating or part that is still gummy? At what precise point in the curing process does the hazard become merely a nuisance dust and no longer an MDA concern? Also we must decide on the best method for waste disposal. Will it be autoclaved, sent to a sanitary landfill, or included in the hazardous waste? And lastly, when is someone going to invent the truly impervious glove called out on the Material Safety Data Sheets?

In summary, we have examined a number of processes which can involve MDA-containing materials, particularly composites. We have discussed exposures that may be expected, possible controls, and reasonable personal protective gear for each. I have emphasized the importance of wipe sampling, and focused special attention on the filament winding process, and emergency response, and added some comments on special problems. Though MDA has its own set of special problems, it is like any other chemical in that it can be used safely with resourcefulness in controls and a commitment to the health of the worker.

SUGGESTED STRATEGIES IN TESTING FOR PULMONARY ABNORMALITIES IN PERSONNEL WHO WORK WITH COMPOSITES

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ABSTRACT

The Presenters appreciation of the Navy experience with composite materials as encountered at the Navy Aviation Depot, North Island (NADEP, NI) points to two sources of potential pathological exposure: 1) respirable dust, encountered when grinding/sanding portions of the graphite epoxy laminate in aircraft, and 2) fumes/vapors which are generated when the heat blanket method of performing localized repairs to the core adhesives becomes excessively exothermic.

The International Association for Research on Cancer (IARC) June 87 Working Group results and other pertinent studies relative to ascribing a pathologic role for inhaled fibers relative to lung cancer, mesothelioma, and fibrotic disease are reviewed. Although little evidence exists which would allow one to infer significant toxicity, information is quite scant. Suggestions on performing surveillance on composite workers are proposed. These recommendations are made assuming the outcome for this worker is most likely to be negative for abnormalities because of low levels of dust exposure.

Finally, a strategy towards the situational physical evaluation that is warranted when an individual is exposed to fumes/vapors in an excess exothermic reaction is outlined.

INTRODUCTION

Composite structures, due to their superior strength to weight ratios and relative ease of fabrication to precise specifications, have enjoyed increased use in Naval Aviation over the past decade. At the Navy Aviation Depot at North Island, this change has been demonstrated as an increased repair/rework load on the F/A-18, which is ten percent composite by weight, and the F-14, which is approximately one percent composite by weight. The principal focus of this paper will concern the Navy rework environment and recommendations regarding the role of occupational medicine (OM) professionals (physicians, nurse practitioners, physician's assistants and occupational health nurses) in

protecting the pulmonary health of workers exposed to composites in this environment. I will also discuss the principles involved in programs that are aimed at preventing systemic and skin toxicity. Finally, I must state that the amount of research into the industrial hygiene data relative to exposure characteristics was very limited due to the short time frame in preparation of this paper. Incomplete exposure characterizations and exposure assumptions are stated. Although most of the conclusions and recommendations are felt valid despite these limitations on exposure data, the reader is urged to study the proceedings from the rest of this conference and judge whether my recommendations still hold up.

RESULTS

The Naval Aviation Depot, North Island, is the largest of six Rework Facilities in the Navy system. Approximately 30 percent of its work involves the F/A-18. Composite work involves working with the "prepreg" resin coated graphite--and in some cases boron--fiber rolls, cutting these, usually using automated cutting equipment, and curing the laminate/fiber material to make replacement parts. In many cases, the composite materials are not replaced; the damaged part is removed by grinding and then patched. Despite this concentration of work on the F/A-18, as a rule, less than three hours a month is spent by any of the ten composite fabricators grinding the composites. Fine black dust is generated in this process, and a reasonably effective ventilation booth with side draft and HEPA filter system are used. In addition, personnel are required to wear respirators. The Navy Environmental Health Center's recommended action level is 3 fibers/cc. Industrial hygiene staff supporting the North Island facility have encountered difficulties in performing fiber counts. It appears that while mishaps with high temperature pyrolysis generate respirable fibers--as was demonstrated from NASA-Ames pyrolysis data--mishaps with low temperature pyrolysis generate larger non-respirable fibers. During grinding dust is primarily produced rather than fibers.[a] Moreover, the respirable fibers that are produced during any of the above settings are significantly reduced in number due to the well known characteristic of these fibers to electrostatically clump together

[a]Low temperature pyrolysis information was derived from LT Formisano's talk while information regarding dust being primarily generated during grinding was derived from several abstracts from Tuesday's lecturers.

In addition to the dust exposure, two other exposures of note occur. Contact with the diglycidyl ether bis-phenyl A epoxy resin system which resulted in an allergic dermatitis in two individuals over the last eight years at the Navy Aviation Depot, North Island (in one case a permanent job transfer was necessary). And, the increasing frequency of use of a high temperature resin system which uses 4,4'-methylene dianaline (MDA) as a curing agent. MDA is a known animal and suspect human carcinogen (NIOSH, 1986). In addition, there are multiple case reports of worker groups with skin contact developing acute hepatitis (ACGIH, 1986).

Finally, while not a routine exposure, the occurrence of resin exotherms with the generation of irritating fumes occurs on the average of about once per year. It seems reasonable to assume this will happen again.

With the above information regarding workplace exposures at the Naval Aviation Depot, North Island, I move on to a review of known epidemiological and toxicological data on these types of fibers. An excellent review on animal toxicological and human epidemiologic data of Man Made Mineral Fibers (MMMF) was presented in the April 1988 American Review of Respiratory Disease (Lockey, 1988). Composite fibers are generally lumped under the category of amorphous continuous filaments. This category, which includes composite fibers and continuous filaments for textiles, was one of three evaluated by IARC in its June 1987 Working Group which reviewed animal toxicology cancer data. The other two groups evaluated are amorphous wool--which includes rock wool, slag wool, and glass wool--and semi-crystalline ceramic fibers for high temperature insulation. Figure 1 summarizes their findings. The data on amorphous continuous fibers, including composite fibers, were classified as "inadequate".

With regard to cancer in humans, the only probable human lung cancers were found in a sub-cohort of workers involved in the early production of rock wool/mineral wool (RW/MW) before dust suppression measures were used (i.e., of a sub-cohort of 331 RW/MW workers taken from a total cohort of 21,976 workers representing all three groups of MMMF exposure, there were 10 lung cancers observed with 3.9 expected for an SMR of 257 ($p < .05$)). Exposures in this group were far greater than the current range of respirable MMMFs which are in the range of 0.01 and 0.1 f/cc.

- AMORPHOUS WOOL TYPE FIBERS
  Rockwool- "LIMITED"
  Slagwool- "INADEQUATE"
  Glass wool-"SUFFICIENT"
- AMORPHOUS CONTINUOUS FILAMENTS-"INADEQUATE
  For TEXTILES
  For REINFORCING PLASTICS
- SEMICRYSTALILLINE CERAMIC FIBERS-"SUFFICIENT"
  For HIGH TEMPERATURE INSULATION

Ca potential judged from animal studies

Figure 1. MMMF epidemiology review. June 1987 IARC Working Group.

With regard to fibrosis in humans, data are scant. The only positive nonmalignant finding related by the authors was a study of 1028 male workers at seven U.S. production plants in which there was an association between duration of work and small opacities on chest x-rays found in a sub-group of smokers with greater than 20 years since first exposure

DISCUSSION

The question now can be addressed regarding the role the occupational medicine (OM) professional can play in protecting the respiratory health of workers. I will also address systemic and dermal concerns. With regard to the protection of workers from potentially toxic exposures, OM professionals perform the following functions. They evaluate individuals prior to placement in jobs that have hazardous or potentially hazardous exposures to chemical, physical, mineral or biologic hazards and certify that individuals do not have any pre-existent illness such that exposure to even low levels of these agents could significantly compromise physical functioning. They assist safety professionals in establishing physical suitability to wear respirators or in providing refractions so that individuals requiring glasses have properly prescribed safety glasses--this is primary prevention. Another form of primary prevention is the assistance provided to safety professionals and management in educating the worker regarding hazards of exposure. They perform periodic medical and laboratory evaluation on individuals, i.e., the performance of physical examinations and tests as required by law or recommended by such public health advisory groups as NIOSH for the purpose of detecting disease at the subclinical state--this is secondary prevention (legally these exams are referred to as medical surveillance and legally such exams include classically defined medical surveillance as well as biological monitoring such as is the case with lead). When an unexpected overexposure to a toxic agent occurs, OM professionals perform situational exams; they attempt to quantitate the exposure in coordination with industrial hygienists and evaluate the individual exposed for obvious physical and subclinical laboratory abnormalities.

The concept of performing periodic exams that serve as a prevention function on workers exposed or potentially exposed to toxic agents implies the performance of medical surveillance exams. In occupational medicine, a great many exams are performed that are motivated more by legal requirements than by their pure worth in prevention. Because of this fact, further examination of the function and motivation behind medical surveillance exams

and, more generally, medical screening exams is warranted. The Journal of Occupational Medicine devoted two issues to the topic of medical screening in 1986. One article on human monitoring contained this pertinent discussion relevant to medical surveillance, "Medical surveillance tests are generally diagnostic tools used in routine medical practice. They include x-ray films, pulmonary function tests, routine blood analysis... Especially if a disease is reversible or arrestable, medical surveillance may be preventive insofar as it serves as a warning sign prompting timely action to avoid future exposures and continuing or progressive adverse health effects." (Ashford, 1986). Dr. Ashford goes on to state "Medical surveillance is most useful in three situations: (1) if compliance with the permissible exposure limits established by OSHA will not adequately ensure worker health; (2) if air measurement cannot sufficiently monitor worker exposure (e.g., if a significant route of entry is not inhalation); and (3) if high-risk groups are exposed."

In the lead article to this series, Dr. Halperin and co-authors, after reviewing some benchmark articles on medical screening, proposed, "a revised set of principles for medical screening in industry...For the purposes of this paper, the goals of screening are assumed to be (1) the early detection and therapy of disease; (2) the evaluation of the adequacy of exposure control and other means of primary prevention; (3) the detection of previously unrecognized health effects suspected on the basis of toxicologic and other studies; and (4) suitable job placement" (Halperin, 1986). Medical screening principles as proposed by Dr. Halperin expand somewhat the medical surveillance guidelines offered by Dr. Ashford and are appropriate in an industry where dust exposure has not been well-clarified and in which new processes and chemicals are being introduced into the workplace.

I want to end my general discussion concerning issues relevant to medical screening--for the rest of this paper I will use medical monitoring synonymously with medical screening--by relating a presentation by Dr. Dean Baker in which he discusses mass psychogenic illness as it relates to worker groups suddenly developing physical symptoms and complaints.[b] Dr. Baker relates three key components: 1) underlying stress, 2) a precipitating event which leads to 3) a crisis of concern. I believe there is potential for such a problem to be significant in an industrial setting, particularly where management often makes strong production

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[b]personal communication with Dr. Baker, Residency Director, Preventive Medicine program, UCLA School of Medicine, 1985.

demands on labor, thus leading to underlying stress. Precipitating events can be a change in work process or merely the simultaneous public concern of key workers regarding the medical effects of a certain exposure, e.g., the black dust generated by grinding. A crisis of worker concern could occur if there were not an optimal relationship between management/medical/safety and the labor group. Prevention strategies would best consider the creation of "mass psychogenic illness" as a distinct possibility.

With the above general considerations in mind, I can now discuss OM testing to be performed on workers at aviation depots as related to known epidemiologic and toxicologic data by making the following assumptions:

1) Eight-hour time-weighted average exposure to respirable composite fibers and dust are not now, and won't be in the foreseeable future, greater than 0.05 f/cc and 0.3 mg/cc[c].

2) Composite fabricators will continue to use MDA as a curing agent; such use will probably increase.

3) Epoxy resin systems with potential dermal sensitizing effects will continue to be used indefinitely.

4) The potential for resin exotherms even with such controls as inert gas autoclaves will remain.

The above assumptions, with the possible exception of the first, also hold true for the manufacturing setting. A final statement regarding the recommendations concerning human monitoring is related, "Human monitoring should be used only if (1) given the specific workplace problem, monitoring serves as an appropriate preventive tool; (2) it is used in conjunction with environmental monitoring; (3) the tests are accurate and reliable and the predictive values are high; (4) it is not used to divert resources from reducing the presence of toxic substances in the workplace or from redesigning technology; and (5) medical removal protection for earnings and job security is provided" (Ashford, 1986). The above discussion and assumptions now allow me to propose the following medical monitoring guidelines:

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[c]0.3 mg/cc of respirable crystalline silica. Silica is doubtlessly a more toxic substance than dust generated from graphite epoxies so that using such a value as a time-weighted exposure action level as well as .05 f/cc time weighted action level for fibers, provides a built-in margin for safety.

1) Composite workers should receive an annual exam that includes pulmonary function testing. Unless workers are to be exposed to concentrations of respirable fibers and graphite dust that exceed an "action level" of greater than 0.05 f/cc or 0.3 mg/cc per hour on a time-weighted average basis.

2) Composite workers should receive an annual monitoring exam. The exam should focus on the eyes, respiratory system and skin. The exam can be a time for the OM professional to emphasize skin precautions. Periodic pulmonary function tests (PFTs) shouldn't be performed, in my opinion, unless the above recommended "action levels" are exceeded. Human epidemiology data previously cited indicated a low fibrogenicity potential-- with concomitant effects on FEV1 or FVC depending on whether the site of fibrogenesis action is at the bronchiolar level as with silica or alveolar level with asbestos--for composite MMMFs. At low exposure levels the predictive value of PFTs would be exceedingly low. Periodic x-rays should not be performed, as the cancer potential seems negligible under any current exposure scenario and only B-Reader interpreted x-rays are felt to have any use in detecting early interstitial lung disease. Recent review of 105,000 radiographs taken of U.S. Navy employees who are exposed to asbestos has demonstrated a 300-fold prevalence range of perceived "definite" parenchymal abnormalities (Ducatman, 1988). The questions this article raises on the accuracy and reliability of such a test, combined with the low predictive value which is reasonably inferred--as fibrosis is truly an unlikely outcome, combine to make B-Reader interpreted radiographs of dubious value for monitoring purposes.

3) Workers who work around composite dust at or above the previously mentioned "action levels" should be certified to wear respirators. NIOSH in their Respirator Decision Logic Monograph (NIOSH, 1986) does not recommend the routine use of chest x-rays or PFTs in respirator certification exams, as such testing contributes little to fitness determination.

4) Workers who are to be in contact with MDA should be on a medical surveillance program as recommended by NIOSH (NIOSH, 1986). This monitoring would include liver function studies and also possible biologic monitoring for MDA and its metabolites, the protocol for which is referenced in the NIOSH Monograph (NIOSH, 1986). I again propose a conservative "action level" of potential skin contact of at least eight hours per month. To await the outcome of the standard setting process for MDA to begin monitoring, in light of known toxicity and suspected carcinogenicity, seems totally unjustified.

In summary, acknowledging incomplete exposure characterization, there is currently no exposure to composite fibers, plastic resin systems, or catalysts which exceeds the action level for legally mandated medical surveillance. I have conservatively defined "action levels" based on a review of the animal toxicity data and epidemiologic data for MMMF. Based on recommendations made by Dr. Halperin of NIOSH (Halperin, 1986) and on other factors I

have elucidated, I feel there is a well-reasoned basis for performing baseline exams prior to placement of composite workers as well as performing annual physical monitoring exams; in the case of MDA exposure, moreover, I believe certain procedures need be performed which meet the first two of three reasons proposed by Dr. Ashford for performing medical surveillance. With the exception of MDA, the predominant emphasis of these exams is a brief history and physical exam and the reinforcement by the OM professional on the needs for careful work practices and the use of PPE. Such periodic exams meet all the goals of medical monitoring listed by Dr. Halperin and, provided x-rays and PFTs are not performed annually, these monitoring exams don't violate the third caveat listed by Dr. Ashford relating to the need for accurate and reliable tests with adequate predictive values.

I close by making three additional points which relate to information discussed in this section. The first relates to the situational problem represented by resin exotherm. I believe there is a slight possibility, if the exposure was significant, for the exposed worker to develop the reactive airway dysfunction syndrome (RADS) defined in my other paper. A preplacement exam can establish a good baseline PFT for the specific worker; annual medical monitoring, I believe, encourages worker contact with the OM professional, should such a situational exposure occur. The second postulate I make is that contact with informed, caring medical professionals minimizes the group worker distress and work disruption that can occur in the "psychogenic illness" situation. My final point relates to emphasizing three of the five caveats listed by Dr. Ashford that I have yet to mention in the test (i.e., the need for environmental monitoring, the preeminent priority of utilizing resources first towards engineering controls and hazards substance substitution, and the need for worker removal protection). Management and supervisory staff must be aware of the preeminence of these priorities if the OM professional is to be successful in the medical monitoring program I have proposed.

REFERENCES

1) ASHFORD, N. A., Policy Consideration for Human Monitoring in the Workplace, Journal of Occupational Medicine, Vol. 28, 563-568. 1986.

2) BURGESS, W. A., Recognition of Health Hazards in Industry, A Review of Materials and Processes, John Wiley & Sons, New York, 1981.

3) DUCATMAN, A. M., YANG, W. N., and FOREMAN, S. A., "B-Reader' and Asbestos Medical Surveillance, Journal of Medicine, Vol. 30, 644-647, 1988.

4) HALPERIN, W. E., RATCLIFFE, J., et al., Medical Screening in the Workplace: Prospered Principles, Vol. 28, 547-552, 1986.

5) LOCKEY, J. E., SHANKER, M. B. et al., Current Issues in Occupational Lung Disease, Journal of Occupational Medicine, Vol. 138, 1047-1050, 1988.

6) American Conference of Governmental Industrial Hygienist, Documentation of TLVs and BEIs, Cincinnati, Ohio, 1986.

7) NIOSH, 4-4'Methylenedianilane (MDA), Current Intelligence Bulletin 47, U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 86-115, 1986.

8) NIOSH, Respirator Decision Logic, U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 87-108, 1987.

CLINICAL EVALUATION OF WORKERS WHO HAVE FILED CLAIMS FOR WORKERS' COMPENSATION FOR ILLNESS POSSIBLY RELATED TO WORK WITH COMPOSITE MATERIALS

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ABSTRACT

A panel of physicians, including specialists in occupational medicine and toxicology, allergy and immunology, and psychiatry, was established to evaluate 37 workers from three plants of an aircraft manufacturing company who filed claims for illness possibly related to work with composite interior airplane parts. Over one-third of the workers had historical symptoms or signs indicative of probable skin or respiratory tract irritation related to work with phenolic or epoxy resin impregnated composite materials. These symptoms are compatible with the known potential toxicity of these materials. The majority of the workers had symptoms compatible with sensory irritation (such as a headache or mild nausea) related to work with composite materials, particularly the phenol-formaldehyde resin materials which are associated with a pungent, unpleasant odor. There was an absence of objective findings indicative of specific organ system impairment or disease to account for most of the systemic symptoms experienced by these workers. Industrial hygiene data did not indicate exposures likely to have produced the myriad systemic symptoms in these workers based on a direct toxic effect of exposures Seventy-three percent of workers met medical criteria for a diagnosis of anxiety (panic disorder) and depression. Most of the physical symptoms (such as headache, nausea, rapid heart beat, difficulty concentrating and remembering, fatigue, chest discomfort, irritability) are likely to have been caused by moderate to severe anxiety and depression. Most of the workers with a diagnosis of anxiety and depression have not received adequate treatment for these disorders. If specific treatment is given, most of the workers are likely to experience significant improvement in their physical symptoms. Such treatment should focus on a return to active life, rather than withdrawal and avoidance.

It is not clear whether the high prevalence of anxiety and depression seen in these workers is due to very low-level exposure to phenol, formaldehyde or organic solvents and associated sensory irritation of the respiratory tract. It is possible that other sociologic factors (such as fear, distrust, misinformation from health care providers, group interaction,

attorney/media involvement, or labor-management problems) are playing a major role in producing or exacerbating these workers' symptoms. To address this concern, it is necessary to study the prevalence of anxiety and depression in a similarly exposed group of workers and matched controls in a workplace that is not "contaminated" by these other sociologic factors.

BACKGROUND

In early 1988, several workers from a large aircraft manufacturing facility consulted a local allergist, known in the area for his frequent diagnosis of systemic formaldehyde poisoning and allergy with organic brain damage. The allergist represented himself to the workers and the local media as an expert on the health effects of occupational and environmental exposure to chemical substances; however, he has no formal training in occupational medicine or toxicology. Following the diagnosis of "reaction to chemicals," a local union representative, himself a patient of the allergist, triaged almost all composite workers with a variety of systemic symptoms to the allergist. This physician announced to the media the presence of a new disease called the "aerospace syndrome" and pronounced it the most serious illness epidemic that he had ever seen. Most of the workers related the onset of their symptoms to the large-scale introduction of phenol-formaldehyde resin impregnated composite materials into the workplace in mid-1987.

Because of the persistent and variable symptoms presented by a group of approximately 40 composite materials workers, and the workplace fear and concern generated by these workers' complaints, the aircraft manufacturing company and their workers' compensation insurance administrator contacted the author to convene a panel of experts to clinically evaluate these workers.

PROCEDURE

Each worker was initially seen by an occupational medicine specialist/internist and an allergist/immunologist. A detailed occupational and medical history was obtained, and a physical examination, including a detailed neurological examination, was performed. Past medical records were reviewed. Blood was drawn for liver, kidney and thyroid function studies, electrolytes, complete blood count with differential, and antibodies to formaldehyde complexed to human serum albumin (HSA). In addition to the blood studies, a urinalyses

and screening spirometry was performed. Each worker also filled out an MMPI questionnaire, which was computer scored with software distributed by Applied Innovations, Inc.

Each of the 37 patients completed a series of self-report questionnaires followed by a structured psychiatric diagnostic interview lasting approximately one hour. Psychiatric interviewers were unaware of any results of the previous evaluations, including the medical examination, MMPI results or information from medical records.

The self-report questionnaires included the following items:

1) The Hopkins Symptom Checklist 90, Revised (SC90R), a symptom checklist on which respondents report the presence and severity of a wide variety of physical and psychological symptoms. The questionnaires assess the current level of psychologic distress in a variety of areas.

2) The Whitely Index, an attitude questionnaire measuring beliefs about illness designed to assess the tendency to show "abnormal illness behavior" (over-reporting of symptoms, excessive seeking of medical care).

3) The Barsky Amplification Scale, a questionnaire measuring the tendency to be overly aware of physical sensations and to report more symptoms than average.

4) The Alameda Disability Questionnaire, a measure of self-perceived current disability and future function.

5) Two additional questionnaires created for this study were a checklist of common physical symptoms (including symptoms of irritant exposure) and a questionnaire asking specifically about "multiple chemical sensitivity" (symptoms in response to a wide variety of environmental stimuli).

The psychiatric examination was a highly structured diagnostic interview developed by the National Institute of Mental Health to assess prevalence of psychiatric illness in community studies. The interview allows only minimal discretion by the interviewer, but cannot completely eliminate bias. It assesses an exhaustive array of physical and psychological symptoms (both current and past) and attempts to exclude other possible causes before attributing any symptom to a psychological cause. One section of the interview intensively reviews past medical information to assess the respondent's tendency toward somatization, which is the propensity to present with recurrent, medically unexplained physical complaints. Interview scoring yields current and lifetime psychiatric diagnoses

according to the criteria of the American Psychiatric Association's Diagnostic and Statistical Manual of Mental Disorders, Third Edition, Revised (DSM-III-R).

After initial evaluation by the above specialists in occupational medicine, allergy/immunology and psychiatry, selected workers were evaluated by a specialist in dermatology, or underwent more detailed neuropsychological testing.

EXPOSURE DATA

Extensive industrial hygiene measurements had been performed since introduction of the phenol-formaldehyde resin material by the aircraft manufacturing company in mid-1987 Since the onset of employee complaints, the Washington Department of Labor and Industries and the National Institute for Occupational Safety and Health had also performed extensive industrial hygiene measurements of employee exposure.

Most of the workers had potential skin and respiratory tract exposure to the following materials used in layup of composite materials:

- Particulates: fiberglass, graphite and Kevlar®
- Phenol
- Formaldehyde
- Organic solvents: styrene, methyl-ethyl-ketone, acetone, xylene, ethylene glycol
- Antimony trioxide
- Tetrabromobisphenol-A
- Epoxy resins
- Trace heavy metals

The concentrations of the above materials in the air were measured at levels a small fraction of the permissible exposure limit for each material that is measurable in air. Details of this exposure will appear in another publication. No trimellitic anhydride, isocyanates, methylene-dianiline, or cobalt were noted by the aircraft manufacturer to be present in the composite materials.

SUMMARY OF THE CLINICAL FINDINGS

A total of 37 composite workers were examined by the medical panel. Among this group the following findings were noted:

1) Fourteen workers reported a past history suggestive of contact dermatitis. No worker had differentiation of allergic or irritant dermatitis with specific patch testing. Only two workers had objective evidence of probable contact dermatitis at the time of the panel exam.

2) Eighteen workers reported a history of subjective symptoms consistent with sensory and mucous membrane irritation of the eyes and/or upper respiratory tract. Only two workers had evidence of mucous membrane inflammation at the time of the panel exam. Both of these workers had evidence of atopic disease.

3) Nine workers reported symptoms consistent with lower respiratory tract irritation. One worker, without a history of atopy, demonstrated bronchial hyperactivity on methacholine testing. This worker had evidence of lower airway hyperactivity that was probably due primarily to exposure to organic solvents and/or particulates in the workplace. Four other workers had objective evidence of airway reactivity, primarily on the basis of pre-existing atopic disease or intrinsic asthma. Most of the latter group experienced temporary exacerbation of symptoms due to the above occupational exposures.

4) Twenty-one workers had subjective symptoms of sensory irritation (such as headache and nausea) that correlated in time with their reported exposure to phenol, formaldehyde, organic solvents, and/or particulates. None of these workers had objective findings correlating with symptoms.

5) Five workers had a history of one or more episodes of autonomic hyperactivity (such as fainting or hyperventilation) correlating in time with exposure to phenol-formaldehyde or other chemicals at work. No worker had objective evidence of permanent organ system impairment related to such an episode on examination by the panel.

6) Three workers reported unphysiologic subjective loss of sensation in a stocking or glove distribution on examination. No worker had objective evidence of peripheral neuropathy on physical examination.

7) Ten workers reported multiple somatic complaints on reported exposure to phenol, formaldehyde and other chemicals at work, as well as reporting similar symptoms while driving in traffic, walking into newly carpeted buildings, reading the newspaper, or other nonoccupational exposure to low levels of diverse chemical substances. None of these workers had objective findings on examination by the panel physicians to account for most of their symptoms

8) Twenty workers had clinical symptoms consistent with a DSM-III-R diagnosis of major depression. Twelve of these workers had new onset of depression correlating in time to work in a particular area of an aircraft manufacturing plant and exposure to materials at work. Eight had previous episodes of depressive illness prior to work in a particular area of an aircraft manufacturing company.

9) Fourteen workers reported symptoms consistent with a DSM-III-R diagnosis of panic disorder or anxiety attacks which correlated in time with work in a particular area of the aircraft manufacturing company. Two had previous episodes of panic disorder.

10) Twenty-one workers had some indication in the medical records that they had tests for antibodies to HSA-formaldehyde, HSA-trimellitic anhydride and HSA-isocyanates. (These tests were performed by Antibody Assay Laboratories, a commercial laboratory operated by Dr. Alan Broughton and associates.) Where results were available, HSA-formaldehyde IgG antibody titers ranged from 1:4 to 1:16. HSA-formaldehyde IgE antibodies were all 1:4. IgM antibodies ranged from 1:4 to 1:32.

DISCUSSION AND RECOMMENDATIONS

A substantial proportion of the workers who have filed workers' compensation claims have histories suggestive of contact dermatitis and/or upper respiratory and eye irritation. These symptoms, and histories of objective findings, are compatible with the known toxicity of the compounds to which the workers were exposed (formaldehyde, phenol, organic solvents, epoxies, particulates, etc.) and the concentrations to which they were exposed (assuming that exposures may have been higher at times prior to the industrial hygiene measurements of the spring of 1988, or that peak exposures were possible in the confined spaces of some of the larger tools, or that skin contact more likely when gloves were not worn routinely). Most workers did not have objective evidence of permanent impairment of the skin or respiratory tract when examined by the multi-disciplinary panel in the fall of 1988

Other workers had histories compatible with one or more episodes of autonomic hyperactivity (nausea, dizziness, shortness of breath, palpitations, syncope, etc.), most probably precipitated by fear or the perception of "toxic" exposure, rather than a direct toxic effect of phenol, formaldehyde or other low-level chemical exposure on the central nervous system. As we will note later, certain individuals may have an abnormal sensitivity to sensory irritation from low-level chemical exposure.

Many of the aircraft manufacturing company workers have health complaints that are not compatible with the known toxicity of the materials at the concentrations to which the workers were likely exposed.

There are few laboratory studies that have any utility in assessing whether formaldehyde exposure may be related to the workers' symptoms. Determination of formic acid blood levels are not useful in assessing systemic absorption of formaldehyde. Patch testing, with nonirritating concentrations of formalin, is useful in determining the presence of Type IV delayed hypersensitivity reactions which cause contact dermatitis with skin exposure The open test or the 15-minute closed skin test with 1-2 percent formaldehyde in water may be useful in assessing urticaria, but does not correlate with other skin, respiratory tract or systemic symptoms. Bardana and Patterson have indicated that the presence of antibodies to human serum albumin formaldehyde conjugates cannot, at this point, be interpreted as representing a systemic hypersensitivity to formaldehyde.

There is no good biological indicator of excessive systemic absorption of phenol in individuals. This is because so many nonoccupational sources of elevated urinary phenol levels interfere with the clinical interpretation of this result. Urinary phenol measurements are useful in evaluating systemic absorption of phenol in epidemiologic studies only.

In spite of the fact that the aircraft manufacturing company workers are not likely to have had the intensity and/or duration of exposure to the chemical substances capable of causing the multiple somatic symptoms described by many of the workers, such symptoms nevertheless exist and are a source of distress and concern among these workers, their co-workers and families.

The most striking finding from this group evaluation is the prevalence of a DSM-III-R diagnosis of depression or panic disorder in 73 percent of these workers. Only 22 percent of the total group reported symptoms consistent with pre-existing depression or panic disorders, so that a majority of workers developed psychiatric illness correlated in time with work in a particular area of an aircraft manufacturing plant and reported chemical exposure

If only symptoms predating work in a particular area of an aircraft manufacturing plant and reported chemical exposure are considered, the prevalence rates of pre-existing psychiatric diagnoses were 5 percent for panic disorder, 22 percent for major depression and 22 percent for other. While the prevalence of pre-existing psychiatric diseases is significantly higher than that found in the general population (3-4 percent for depression), it is quite

similar to rates reported for patients visiting general medical clinics (which would be the most appropriate comparison group). Thus, this group of workers who have filed workers' compensation claims display a higher prevalence of current anxiety and depression not well explained by pre-existing psychiatric illness.

Depressed individuals usually present with a variety of physical complaints. Often somatic complaints may be predominant and the usual hallmarks of depression, such as sadness and depressed mood, may be absent. In the majority of this group, somatization appears to have been a recent phenomenon occurring in the setting of major depression or panic disorder.

Our medical investigation has found little objective evidence of organic system impairment in these workers that could be attributed to a direct toxic or immunologic effect of chemical exposure, except for historical evidence of respiratory tract and skin irritation. These latter findings are compatible with the known, usually temporary, toxicity of these compounds. No medical diagnosis exists to explain many of these workers' systemic symptoms. We believe that the high prevalence of psychiatric diagnoses in this group explains much of the systemic symptoms (such as fatigue, difficulty with concentration and memory, sleep disturbances, dizziness, palpitations and fainting spells) as these are commonly seen in depression and panic disorder. This phenomenon of somatization may be a chronic tendency or an acute complication of anxiety or depression.

The high prevalence of panic disorder suggests that there may be significant interaction between the sensory and irritant stimulation of skin and mucous membranes of the upper respiratory tract and the autonomic or central nervous system reaction to such stimulation.

There are reports in the literature of panic disorder being initiated by exposure to organic solvents, or materials such as hydrogen sulfide or chlorine, associated with an irritating or pungent odor. Usually, but not always, such exposure has been associated with a direct toxic effect of chemical exposure with systemic symptoms of acute intoxication such as acute neurological symptoms. Some individuals may have a genetic predisposition to panic disorder, which may be objectively demonstrated by susceptibility to symptom provocation with intravenous lactate infusion or increased concentrations of carbon dioxide in air.

In some individuals, symptoms of mucous membrane or sensory irritation, or the perception of toxic exposure may produce a state of autonomic arousal which leads to a full-blown panic attack and further symptoms of autonomic arousal. Such idiosyncratic nondose-related reactions are not thought to be due to a direct toxic effect of chemical exposure on the central nervous system. In fact, some of the chemicals precipitating these reactions are not readily absorbed systemically (such as hydrogen sulfide, chlorine or formaldehyde) and so direct central nervous system toxicity is unlikely.

Some behavioralists have postulated that a chemical may produce mucous membrane irritation and serve as an unconditioned stimulus for a status of autonomic arousal or panic attack. Subsequent to this, a relatively lower exposure, associated with the chemical's characteristically irritating or pungent odor, becomes a conditioned stimulus for the same response. This Pavlovian type of conditioned response has been termed by Schusterman as "behavioral sensitization to odorant." This author states that this response is protective and adaptive, and has little to do with underlying psychopathology.

Some individuals may simply have extremely low thresholds for perceiving odors or for irritation of sensory receptors. There is a variability in the extent of variation of odor detection among individuals, as well as extent to which individuals experience mucosal irritation when exposed to materials such as cigarette smoke. In addition, vulnerability to symptom development may be increased in certain pre-existing medical conditions such as asthma, allergy or respiratory tract infection. The threshold for irritation also may be lowered by anxiety, fear and depression.

The initial symptomatic episode for some of the workers may have been sensory or mucous membrane irritation from exposure to phenol, formaldehyde or organic solvents. On the other hand, for some, the initial symptoms may be those of autonomic hyperactivity resulting from the fear associated with potential exposure. For yet another group of aircraft manufacturing company workers, symptoms may be unrelated to any chemical exposures, but may mistakenly be attributed to such exposure or potential exposure.

Depression may result from neurotoxic effects of chemical exposure. Such syndromes have been reported in the medical literature. Typically, these studies report neuropsychologic abnormalities following long periods of exposure to levels of chemicals (typically organic solvents) higher than those to which we believe this group was exposed. Most studies have primarily looked at neuropsychologic impairment and only given

secondary attention to psychologic symptoms which might occur with briefer or lower level exposure.

It is clear that major depression, anxiety disorders or a tendency to somatize are likely to be the major cause of most of the systemic symptoms in these aircraft manufacturing company workers. What is not clear is whether psychiatric disturbances and the associated somatic symptoms are a result of low-level chemical exposure and/or the fear of toxicity of such exposures. It is also possible that other sociologic factors (such as health care provider/co-worker/media reinforcement of the perception of illness and illness behavior) may play a major role in the production or exacerbation of these observed psychiatric disturbances, while chemical exposure may have little direct causal relationship.

This outbreak of physical symptoms along with symptoms of anxiety and depression could result from a group process of amplifying symptoms and attributing them to a common cause. A climate of anxiety coupled with a group belief among workers that they were endangered could lead to such a process. Workers under the impression that they were not adequately informed about or protected from health risks would be more susceptible to such "group somatization." No test or investigation could prove that such a process occurred. We can only suspect such an explanation when other causes of such an outbreak have been excluded with reasonable certainty. Of course, such a group process could act in concert with any other mechanism to increase the level of symptoms and illness that would otherwise occur.

In some aircraft manufacturing company employees, symptoms which initially occurred only in response to circumscribed exposures to discrete substances eventually became provoked by exposure to many different types of chemicals and odors not encountered in the workplace. In terms of the behavioral model, stimulus generalization has occurred. These workers resemble a heterogeneous group of patients exhibiting a relatively new, but increasingly common, illness described in the medical literature as "multiple chemical sensitivity syndrome." This is defined as "a chronic (continuing for more than three months) multi-system disorder, usually involving symptoms of the central nervous system and at least one other organ system. Affected persons are frequently intolerant and react adversely to some chemicals and to environmental agents, singly or in combination, at levels generally tolerated by the majority of persons. Affected persons have varying degrees of

morbidity from mild discomfort to total disability. On physical examination, the patient is normally free from any abnormal objective findings."

Ten workers of the total group reported symptoms of multiple chemical sensitivity by questionnaire. These workers had a much higher frequency of pre-existing psychiatric illness (80 percent) and pre-existing tendency to somatization (70 percent) than the remainder of the group. This suggests that the development of the full multiple chemical sensitivity syndrome may be related to prior psychiatric illness or psychologic vulnerability.

In summary, it is clear that the aircraft manufacturing company workers who have filed claims for chemical exposure are a heterogeneous group. The majority of these workers show evidence of anxiety and depression associated with work in a particular area of an aircraft manufacturing company plant. Whether these psychiatric symptoms are caused by neurologic effects of low level chemical exposure, or the sociologic effects of chemical fear, they have clearly caused much distress and functional disability. Depression and anxiety both increase the frequency and severity of physical symptoms. Fortunately, specific and effective treatments can relieve the psychiatric and physical distress All clinical experience points toward rebuilding health and return to active life. The avoidance of all chemical exposures recommended by some health care practitioners only perpetuates illness and reinforces disability. Of course, this approach needs to be combined with strict engineering controls, work practices and use of personal protective equipment to minimize skin and respiratory tract exposure to the chemicals present in the aircraft manufacturing company plants.

Evidence in the medical literature to date does not support a causal relationship between these workers' exposure to low levels of phenol, formaldehyde, organic solvents and other chemicals in the development of (or exacerbation of pre-existing) psychiatric disturbances such as depression, panic disorder or a tendency to report more somatic symptoms than the average person. Neither does the literature support a causal relationship between immune parameters, such as low titers of antibodies to HSA-formaldehyde, and the development of symptoms in multiple organ systems in these workers.

It is not clear, however, whether there are factors in the workplace, including, but not limited to, chemical exposure, that may cause these workers to express more psychiatric illness than would be expected without such workplace contact. Such questions simply

cannot be answered by evaluating only those workers who have filed workers' compensation claims for illness.

Further investigation is clearly needed to answer two questions:

1) Do composite plastic workers have a higher prevalence of psychiatric symptoms and psychiatric illness compared with a comparable group working with other materials?

2) Do workers exposed to low levels of these chemicals in settings where sociologic factors differ (contact with providers/union/media, etc.) show a similarly high prevalence of psychiatric symptoms?

These questions seem unanswerable through further investigation of the particular aircraft manufacturing company work sites involved in our evaluation. It may be addressed, however, in a work site-based epidemiologic study of the prevalence of psychiatric dysfunction in workers exposed to phenol-formaldehyde and other composite materials, and appropriate controls, in a work site that has not experienced the sociologic factors of the mass filing of workers' compensation claims, attorney involvement and adversary relations between labor and management, as well as the reinforcement of illness behavior and fear of serious illness by practitioners, co-workers and others.

It is recommended that the tools of assessment of cognitive function include those designed to assess psychiatric dysfunction (such as those used in this evaluation). If standard neuropsychological testing is used, we suggest that a shortened version (using parameters previously shown to be affected by solvent exposure) be used as a screening battery in an epidemiologic investigation in conjunction with the psychiatric assessment

In order to answer questions related to immune system function, it is also necessary to perform a work site-based epidemiologic study. This study should thoroughly evaluate worker exposure, as well as parameters of immune function, in exposed symptomatic workers, a matched group of exposed asymptomatic workers, and a matched group of workers without exposure.

ANNOTATED BIBLIOGRAPHY

ADAMS, R.M. (1983). Occupational Skin Disease. Grune and Stratton, New York

ALARIE, Y., L. KANE AND BARROWS, C.S. (1981). Sensory irritation: The use of an animal model to establish acceptable limits to airborne chemical irritants. In Toxicology Principles and Practices (A.L. Reaves, ed.) Vol. I. John Wiley & Sons, New York.

AMERICAN PSYCHIATRIC ASSOCIATION. (1987). Diagnostic and statistical manual of mental disorders, revised. Washington, DC.

ANDERSON, I. AND MOLHAVE, L. (1983). Controlled human studies with formaldehyde. In Formaldehyde Toxicity, Chapter 14 (J.E. Gibson, ed). Hemisphere, New York.

AXELSON, O., HANE, M., AND HOGSTEDT, C. (1976). A case-referent study on neuropsychiatric disorders among workers exposed to solvents. Scand J. Work Environ. Health. 2, 14.

AXELSON, O., HANE, M., AND HOGSTEDT, C. (1980). Current aspects of solvent-related disorders. In Developments in Occupational Medicine (C. Zenz, ed) Year Book, Medical Publishers, Chicago.

BAKER, E.L. AND FINE, L.J. (1986). Solvent neurotoxicity: The current evidence. J. Occup. Med. 28, 126.

BAKER, E.L., LETZ, R., AND FIDLER, A. (1985). A computer-administered neurobehavioral evaluation system for occupational and environmental epidemiology. J. Occup. Med. 27, 206.

BAKER, E.L., JR., SMITH, T.J., AND LANDRIGAN, P.J. (1985). The neurotoxicity of industrial solvents: A review of the literature. Am. J. Ind. Med. 8, 207.

BARDANA, E.J. AND MONTANARO, A. (1987). The formaldehyde fiasco: A review of the scientific data. Immunology & Allergy Practice. 9(1), 11.

BARRETT, J.E., BARRETT, J.A., OXMAN, T.E., AND GERBER, P.D. (1988). The Prevalence of Psychiatric Disorders in a Primary Care Practice. Arch. Gen. Psychiatry 45, 1100.

BARROW, C.S., STEINHAGEN, W.H., AND CHENG, J.C.F. (1983). Formaldehyde sensory irritation. In Formaldehyde Toxicity, Chapter 3 (J.E. Gibson, ed.). Hemisphere, New York.

BECK, A.T., WARD, C.H., MENDELSON, M., et al. (1981) An inventory for measuring depression. Arch General Psychiatry. 4, 561.

BOJA, J.W., NIELSEN, J.A., FOLDVARY, E., AND TRUITT, E.B., JR. (1985). Acute low-level formaldehyde behavioral and neurochemical toxicity in the rat. Prog. Neuro-Psychopharmacol. Biol. Psychiatry. 9, 671.

BOLLA-WILSON, K., WILSON, R.J., AND BLEECKER, M.L. (1988). Conditioning of physical symptoms after neurotoxic exposure. J. Occup. Med. 30(9), 684.

BOXER, P.A. (1985). Occupational mass psychogenic illness. J. Occup. Med. 27, 867.

BRODSKY, C.M. (1983). "Allergic to everything": A medical subculture. Psychosomatics. 24(8), 731

BROUGHTON, A. AND THRASHER, J.D. (1988). Antibodies and altered cell mediated immunity in formaldehyde exposed humans. Common Toxicol. 2(3), 155.

BURGE, P.S., HARRIES, M.G., LAM, W.K., et al. (1985). Occupational asthma due to formaldehyde. Thorax. 40, 255.

CHERRY, N., HUTCHINS, H., PACE, T., et al. (1985). Neurobehavioral effects of repeated occupational exposure to toluene and paint solvents. Br. J. Ind. Med. 42, 291.

CONE, J.E., HARRISON, R., AND REITER, R. (1987). Patients with multiple chemical sensitivities: clinical diagnostic subsets among an occupational health clinic population. In Workers with Multiple Chemical Sensitivities (M.R. Cullen, ed.) Occupational Medicine: State of the Art Reviews. 2, 721.

COWLEY, D.S., DAGER, S.R., AND DUNNER, D.L. (1986). Lactate-induced panic in primary affective disorder. Am. J. Psychiatry 143, 646.

CRIPE, L.I. AND DODRILL, C.B. (1988). Neuropsychological test performances with chronic low-level formaldehyde exposure. The Clinical Neuropsychologist. 2(1), 41.

CULLEN, M.R., ed. (1987). Workers with multiple chemical sensitivities. Occupational Medicine: State of the Art Reviews. 2, 655.

DAGER, S.R., HOLLAND, J.P., COWLEY, D.S., et al. (1987). Panic disorder precipitated by exposure to organic solvents in the workplace. Am. J. Psychiatry. 144, 1056.

DAGER, S.R., HOLLAND, J.P., COWLEY, D.S., et al. (1988). Letter to the editor. Am. J. Psychiatry. 145(4), 532.

DEICHMAN, W.B. AND KEPLINGER, M.L. (1981). Phenols and Phenolic compounds. Patty's Industrial Hygiene and Toxicology (3rd ed) (G.D. Clayton, F.E. Clayton, ed.) Ch. 36, pg. 2567. John Wiley & Sons, New York.

EMMETT, E.A. (1976). Parosmia and hyposmia induced by solvent exposure. Br. J. Ind. Med. 33, 196.

FEINMAN, S.E. (1988). Formaldehyde Sensitivity and Toxicity. CRC Press, Boca Raton, Florida.

FELTON, J.S. (1988). Psychogenic illness in the workplace. Western J. Med. 148, 77.

FLODIN, U.Y., EDLING, C., AND AXELSON, O. (1984). Clinical studies of psycho-organic syndromes among workers with exposure to solvents. Am. J. Ind. Med. 5, 287.

GIBSON, J.E. (ed.). (1983). Formaldehyde Toxicity. Hemisphere, New York.

GREGERSON, P., ANGELSO, B., NEILSEN, T.E., et al. (1984). Neurotoxic effects of organic solvents in exposed workers: An occupational, neuropsychological and neurological investigation. Am. J. Ind. Med. 5, 201.

GUIDOTTI, T.L., ALEXANDER, R.W., AND FEDORUK, M.J. (1987). Epidemiologic features that may distinguish between building-associated illness outbreaks due to chemical exposure or psychogenic origin. J. Occup. Med. 29, 148.

HANE, M., AXELSON, O., BLUME, J., et al. (1977). Psychological function changes among house painters. Scand. J. Work Environ. Health. 3, 91.

HANNINEN, H., ESKELINEN, L., HUSMAN, K., et al. (1976). Behavioral effects of long-term exposure to a mixture of organic solvents. Scand. J. Work Environ. Health. 2, 240.

HENDRICK, D.J., RANDO, R.J., LANE, D.J., AND MORRIS, J. (1982). Formaldehyde asthma: Challenge exposure levels and fate after five years. J. Occup. Med. 24, 893.

KILBURN, K.H., SEIDMAN, B.C., AND WARSHAW, R. (1985). Neurobehavioral and respiratory symptoms of formaldehyde and xylene exposure in histology technicians. Arch. Environ. Health. 40, 229.

KULLE, T.J. AND COOPER, G.P. (1975). Effects of formaldehyde and ozone on the trigeminal nasal sensory system. Arch. Environ. Health. 30, 237.

LETZ, R. AND BAKER, E.L. (1986). Computer-administered neurobehavioral testing in occupational health. Sem. in Occup. Med. 1, 197.

LUSTER, M.I. AND DEAN, J.H. (1982). Immunological hypersensitivity resulting from environmental or occupational exposure to chemicals: A state-of-the-art workshop summary. Fundam. Appl. Toxicol. 2, 327.

LUSTER, M.I., MUNSON, A.E., THOMAS, P.T., et al. (1988). Development of a testing battery to assess chemical-induced immunotoxicity: National Toxicology Program's guidelines for immunotoxicity evaluation in mice. Fundam. Appl. Toxicol. 10, 2.

MAIBACH, H.I. (1983). Formaldehyde: Effects on animal and human skin. In Formaldehyde Toxicity, Chapter 15. The Third Chemical Industry Institute Toxicology Conference. (J.E. Gibson, ed.) Hemisphere, New York.

MCGRATH, K.G., ZEISS, C.R., AND PATTERSON, R. (1983). Allergic reactions to industrial chemicals. Clin. Immunol. Rev. 2(1), 1.

National Center for Toxicological Research. (1984). Consensus workshop report on formaldehyde, Little Rock, Arkansas, October 1983. In Environ. Health Perspect. 58, 323.

NEELY, W.B. (1964). The metabolic fate of formaldehyde -14C intraperitoneally administered in the rat. Biochem. Pharmacol. 13, 1137.

O'DONOGHUE, J.E. (ed.). (1985). Neurotoxicity of Industrial and Commercial Chemicals, Volume II. CRC Press, Inc., Boca Raton, Florida.

PATTERSON, R., DYKEWICZ, M.S., GRAMMER, L.C., et al. (1987). Formaldehyde reactions and the burden of proof (editorial). J. Allergy Clin. Immunol. 79(5), 705.

PATTERSON, R., HARRIS, K.E., STOPFORD, W., et al. (1988). Irritant symptoms and immunologic responses to multiple chemicals: Importance of clinical and immunologic correlations. Int. Arch. Allergy Appl. Immunol. 85(4), 467.

PATTERSON, R., PATERAS, V., GRAMMER, L.C., AND HARRIS, K.E. (1986). Human Antibodies against Formaldehyde-Human Serum Albumin Conjugates or Human Serum Albumin in Individuals Exposed to Formaldehyde. Int. Arch. Allergy Appl. Immunol. 79, 53.

PATTERSON, R., SUSZKO, I.M., ZEISS, C.R., AND PRUZANSKY, J.J. (1981). Characterization of hapten-human serum albumins and their complexes with specific human antisera. J. Allergy Clin. Immunol. 1(3), 181.

PATTERSON, R., ZEISS, C.R., ROXE, D., et al. (1980). Antibodies in hemodialysis patients against hapten-protein and hapten-erythrocytes. J. Lab. Clin. Med. 96(2), 347.

PROSS, H.F. (1987). Immunologic studies of subjects with asthma exposed to formaldehyde. J. Allergy Clinic. Immunol. 79, 797.

SCHOTTENFELD, R.S. (1987). Workers with multiple chemical sensitivities: A psychiatric approach to diagnosis and treatment. In Workers with Multiple Chemical Sensitivities (M.R. Cullen, ed.). In Occupational Medicine: State of the Art Reviews. 2, 739.

SCHOTTENFELD, R.S. AND CULLEN, M.R (1985). Occupation-induced post-traumatic stress disorders. Am. J. Psychiatry. 142, 198.

SCHWETZ, B.A. (1988). Immunotoxicology: An important new subdiscipline of toxicology (editorial). Fundam. Appl. Toxicol. 10, 1.

SHUSTERMAN, D., BALMES, J., AND CONE, J. (1988). Behavioral sensitization to irritants/odorants after acute overexposures. J. Occup. Med. 30(7), 565

STRUWE, G., KNAVE, B., AND MINDUS, P. (1983). Neuropsychiatric symptoms in workers occupationally exposed to jet fuel -- a combined epidemiological and casuistic study. Acta. Psychiatr. Scand. (Suppl.). 303, 55.

TASK FORCE ON CLINICAL ECOLOGY - A CRITICAL APPRAISAL. (1986). West. J. Med. 144, 239.

TERR. A.I. (1986) Environmental illness: A clinical review of 50 cases.. Arch. Intern. Med. 146, 145.

THRASHER, J.D., BROUGHTON, A., AND MICEVICH, P. (1988). Antibodies and immune profiles of individuals occupationally exposed to formaldehyde: S x case reports. Am. J. Ind. Med. 14, 479.

THRASHER, J.D., WOJDANI, A., CHEUNG, G., AND HEUSER, G. (1987). Evidence for formaldehyde antibodies and altered cellular immunity in subjects exposed to formaldehyde in mobile homes. Arch. Environ. Health. 42, 347

ZEISS, C.R., WOLKONSKY, P. CHACON, R., et al. (1983). Syndromes in workers exposed to trimellitic anhydride. A longitudinal clinical and immunologic study. Ann. Intern. Med. 98(1), 8.

VII. HAZARD EVALUATION AND COMMUNICATION

CONSENSUS STATEMENT

A conference goal was to determine whether or not epidemiologic studies of composite workers are needed and, if so, under what conditions. It appears that epidemiologic studies are not appropriate at this time because the causative agents have not been well defined due to multi-chemical exposures, insufficient number of controlled animal experiments, and undefined adverse effects. Considering these limitations, epidemiological studies will probably be extremely expensive and unproductive in determining a cause-effect relationship with composite chemical exposure.

When epidemiologic studies are feasible it must be realized that much larger study populations are required to prove a chemical safe than to prove it is a hazard with the same degree of statistical confidence. The study group size effect is much greater when the disease outcome is extremely rare. Additionally, it must be accepted that exposure indices derived from work history information may be misleading and could bias the study toward finding no effect.

Material Safety Data Sheets (MSDSs) are the primary source for transmitting hazardous material information from the initial manufacturer through the distributors to the final receiver - the worker. MSDSs were not required for hazardous materials for any industries except shipyards until the beginning of the 1980's, although many companies provided MSDSs due to customer demand. The Occupational Safety and Health Administration Hazard Communication Standard, 29 CFR 1910.1200, now requires MSDS in the workplace for all hazardous materials in all industries.

There are a variety of MSDSs, from the two-page OSHA Form 174 to 10-20 page formats. Although an MSDS must be automatically shipped with the first shipment of hazardous materials and whenever the MSDS is updated, enforcement of the OSHA HCS places the burden of obtaining the MSDS on the hazardous material user. This requires the user to establish administrative controls to ensure MSDSs are received.

Quality in MSDSs is a major issue. Often the information appears to be provided strictly to limit the manufacturer's liability. For example, suggested personnel protective equipment is usually the maximum available, regardless of the degree of toxicity of the

product. There is a large degree of variability in the quality of MSDSs, which may be due to some extent to the size of the company preparing the MSDS. For example, smaller companies don't always have familiarity with the references in 29 CFR 1910.1200 and may not have the ability to conduct required testing.

Proprietary information or trade secret information is protected from disclosure; however, to be protected, a trade secret must meet the following criteria:

a. Not previously disclosed.

b. Not required by federal law.

c. Substantial competitive advantage.

d. Not readily discoverable by reverse engineering.

However, trade secret information must be available to health professionals in the event of a medical emergency, or if the information is needed to protect the health of the worker. The health professional may be required to sign a statement of nondisclosure.

Labeling may be the first contact the worker has with a hazardous material. The label must have a name linking it to an MSDS. It must tell the hazard and not be merely a precautionary statement such as "Do not breathe the vapors." The label must also include the name and address of the responsible party. This last requirement is not necessary for inplant labeling systems. Labels should be concise. Lengthy labels are less likely to be read and followed

Workers want to perform their job without getting sick. They want full information on the chemicals with which they are working, the type of personnel protective equipment required, and the type and degree of engineering controls available. If the hazards are not known, the worker must be fully protected until the degree of hazard is defined.

The worker must receive this information through hazard-specific training. Workers desire to actively participate in the development and presentation of the training program and the design of workplace controls. This training must be completed and the engineering controls must be in place before employees begin work with the material. Workers also want their complaints taken seriously and to be involved in the selection of doctors

An effective hazard communication training program contains the following elements:

a. An enthusiastic instructor who is familiar with the work area.

b. Presentation to small groups (less than 20), including the first line supervisor.

c. Encourage questions.

d. Use product handling information sheets which discuss work area specific work practices, personnel protective equipment, engineering controls, any special handling procedures such as maximum temperature, carcinogen designation if appropriate, the phone number of the preparing individual, and the location of additional information.

e. A feedback loop where the trainer visits the employees to determine the effectiveness of the training.

f. An occupational health staff which is willing and available to listen.

In summary, effective occupational health programs are distinguished by good communications between management and the employee which convey management's genuine concern for the employee. One indicator of this concern is a strong, visible occupational safety and health program which participates in the management process and is able to initiate actions to correct poor work facilities and practices.

The Value of Epidemiological Studies

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ABSTRACT

The ongoing Air Force Health Study, the Air Force investigation of health effects in Ranch Hand veterans exposed to Agent Orange and its contaminant, 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), is presented as a model epidemiologic study of occupational exposure to a toxic chemical. The relationship between an exposure estimate, based on total gallons sprayed, and current TCDD body burden in 352 assayed Ranch Hands is presented and discussed. Associated bias calculations are presented.

INTRODUCTION

The role of epidemiology in the resolution of health complaints arising from occupational exposure to advanced composites in manufacturing may be viewed as one step in a scientific process to assess whether adverse health effects exist and, if so, whether they can be attributed to the exposure. Preliminary to an epidemiologic effort, toxicologists and biologists will have studied specific effects in controlled animal experiments and will have hypothesized mechanisms and metabolic pathways for the toxin. Such prior knowledge is indispensable for the planning and conduct of epidemiological studies.

Given that an epidemiologic effort is being contemplated, three cautions must be kept in mind by policy makers and study planners. They are: (1) large epidemiologic studies are statistical investigations, the results of which must be scrutinized with respect to established causality criteria, (2) epidemiologic studies of occupational exposures are generally never large enough to establish safety, and (3) exposure misclassification can severely bias a study toward finding no effect when in fact a substantial health effect exists. These well known concepts are illustrated here with the Air Force Health Study, the Air Force investigation of health effects in Ranch Hand veterans exposed to "Agent Orange".

BACKGROUND: THE AIR FORCE HEALTH STUDY

The Air Force Health Study (AFHS) (1-3) is designed to determine whether members of Project Ranch Hand, the unit tasked with herbicide spray operations during the Vietnam conflict, have experienced adverse health effects and whether those effects, if they exist, can be attributed to their occupational exposure to herbicides or their contaminant (TCDD). The AFHS was initiated by the Air Force in 1978 in response to a request by Congress that the Department of Defense conduct a long term epidemiologic study of health effects in personnel exposed to herbicides. In 1980, the White House formally directed the Department of Defense to initiate a study of Ranch Hand veterans. This decision has subsequently been reaffirmed by succeeding administrations.

The AFHS is a 20-year prospective study of 1261 Ranch Hands and an equal number of matched Comparison Air Force veterans, matched on date of birth, race, rank and occupation. The Comparisons were selected from the population of Air Force personnel who flew and maintained C-130 cargo aircraft in Southeast Asia during the same period, 1961 through 1972, that the Ranch Hand unit was active in Vietnam. These men were physically examined in the baseline year, 1982, and in 1985 and 1987. The next examinations will occur in 1992, 1997 and in the concluding year of the study, 2002. The study has three arms: morbidity, mortality and reproductive effects. The morbidity arm consists of the physical examinations and associated interviewing and laboratory assays on the study participants. The mortality arm consists of annual mortality contrasts of the Ranch Hand cohort and the entire Comparison population of 19,101 individuals The reproductive arm is an investigation of birth defects in all 7000 children fathered by the Ranch Hands and Comparisons seen in the physical examinations.

The second follow-up examination data is currently being analyzed by our prime contractor A report will be released in early 1990. At the same time, Air Force investigators will analyze and report the reproductive effects study, to be released in mid-1990. A new dimension to the investigation has been added by the Centers for Disease Control (CDC) Early in 1987, CDC chemists developed a laboratory assay for TCDD in human serum which they validated against the well established, but invasive, adipose tissue assay, showing that the two methods produce nearly identical results (4). Very soon thereafter, the Air Force collaborated with the CDC to assay 200 AFHS participants, 150 Ranch Hands and 50 Comparisons, to validate Ranch Hand exposures and, with frozen serum from the 1982 examination, estimate the half-life of TCDD in humans. The results (5) show that the Ranch

Hands still possess high body burdens of TCDD approximately 17 years after exposure and that the half-life of TCDD in Ranch Hands is approximately 7.1 years (6). The relatively long half-life means that most Ranch Hands are within two to three half-lives of their Vietnam exposure. The CDC is currently assaying all Ranch Hands and Comparisons who complied with the blood draw during the second follow-up examination in 1987.

At the outset, we faced many complications that limited our ability to detect an effect if one did indeed exist. Our sample size was limited to 1261 Ranch Hands. Thus our statistical power is fixed by nature, precluding study of rare diseases such as specific types of cancer and, especially, soft tissue sarcoma. We anticipated overt and subtle reporting biases that could, if not identified and circumvented, invalidate our results. No known disease endpoint was prespecified. Veteran complaints covered a broad range of medical and psychological conditions as well as a variety of adverse reproductive effects. The physical examinations, interviews, and laboratory assays are therefore wide ranging, producing hundreds of analyzable endpoints, each with its own set of risk factors. The reproductive effects investigation is based on the medical record verification of birth defects in every child fathered by the study participants; it also includes analyses of stillbirths, abortions, infant and prenatal mortality, and physical and mental impairments.

In the hypothetical case that there is no herbicide effect on health, about 5 percent of the many hundreds of statistical tests of hypothesis applied on the same data arising from this study will reject (produce p-values less than 0.05). This is known as the multiple testing artifact and it is common to all large studies. Unfortunately, there is no known statistical procedure that can distinguish between significant group differences that arise due to the multiple testing artifact and those which may arise due to a true herbicide effect. To guard against misinterpreting the multitude of findings, we scrutinize each finding, applying prior knowledge, concomitant information and causality criteria.

The latency periods of adverse health effects, if they exist, are also unknown. Animal experiments have produced results sometimes conflicting with veteran complaints, complicating our efforts to interpret study results. The study is necessarily long, 20 years, to ensure that we will not miss a latency effect if one exists.

Since there was no dosimetry for the Ranch Hands during their tours in Vietnam, we have no direct way to assess their exposure to herbicides or dioxin. We attempted to approximate their exposure with an index based on work history data, following the example of other classic epidemiologic studies. The inadequacy of that index is now being realized.

STATISTICAL ASSOCIATIONS AND CAUSALITY CRITERIA

Large epidemiological studies are necessarily statistical. Without a well defined endpoint, investigators must compare exposed and control cohorts on dozens or even hundreds of medical conditions. Statistical analyses produce measures of association between exposure status (exposed, control) and each endpoint. Additionally, analyses are adjusted for covariates to reduce bias and variance. Analyses will be biased if certain covariates, termed confounders, are not taken into account. The inclusion of covariate information in an analysis also allows the investigation of the change in the exposure versus endpoint association with a covariate.

Due to the multiple testing artifact, investigators must assess many statistical associations to determine which are suggestive of a causal relationship between exposure and health effects and which ones are not. Among those that are statistically associated with exposure, some may be noncausally and some may be causally associated. Causal associations may be indirect or direct. An indirect causal association between a medical condition and an exposure occurs when the exposure causes a change in an intermediate condition and that change causes the medical condition of interest to become manifest. For example, it may be conjectured that exposure to TCDD is indirectly causally related to heart disease through its ability to increase levels of cholesterol.

Interpretations require the combined efforts of medical doctors, statisticians and subject matter specialists. A thorough interpretation will assess significant associations, the directionality of the findings, regardless of statistical significance, and changes in directionality or association with covariate information. Causality criteria have been widely discussed in the literature, see Kleinbaum, Kupper and Morgenstern (7), for example. A minimal set of criteria is (1) time sequence, (2) strength of association, (3) dose response and (4) consistency. To support a causal argument, the exposure must have occurred earlier in time sequence than the medical condition of interest. Even though a study will have identified a group of exposed individuals, the exposure may not have occurred during a fixed time period for some subjects or the medical condition may have precursors that occurred

before the exposure. Causal associations may be stronger than noncausal associations, although strength of association will not be a reliable guide when the exposure is heterogeneous, of short duration, or expressed only after a long latency period. A dose response relationship between exposure and a specific medical condition is sought via the development of an exposure index. Individuals with no exposure should experience fewer conditions than those subjects with low exposure and these, in turn, should have fewer conditions than heavily exposed subjects. In the absence of individual dose information, as is usually the case in studies of occupational exposure, studies rely on indirect indices of exposure, such as cumulative time on the job, to assess the dose response relationship. Finally, if the association is to support a causal argument, it should be consistent with existing subject matter knowledge, usually derived from animal and laboratory experiments.

PROOF OF SAFETY VERSUS PROOF OF HAZARD

In 1985, Bross presented minimal sample size criteria for proof of safety and for proof of hazard in studies of environmental and occupational exposures (8). His work is directed at rectifying widespread misconceptions about proof of safety that are prevalent in government agencies, in the medical and scientific establishments, and in other groups involved in occupational and public health and safety. He cites the erroneous notion that a failure to obtain statistically positive results in an epidemiologic study warrants a claim of safety, such as in EPA interpretations of Love Canal data (9). The conclusion of his work is that it is far more difficult to provide a valid scientific proof of safety than to provide a corresponding proof of hazard. He shows that the quantity of data required for a valid assurance of safety is of the order of 30 times greater than that required for a valid proof of hazard. In fact, the size of the sample needed so far exceeds what is ordinarily available in epidemiologic studies, that assurances of safety given on the basis of such studies have no scientific validity. Bross's work was later refined and extended by Millard (10).

Bross's work, summarized here in terms of relative risk, requires the simplifying assumptions that a specific change occurs in the environment or workplace at a known time in a given place within a stable population. The change might be an accident or a technological innovation in the workplace. The population at risk is assumed observed for equal time intervals before and after the event or, in studies with a control group, that the person-time of follow-up in the two groups are equal. Let the adverse health effects be called "deaths". Let the number of deaths in the "before" period be x and in the "after" period

be y. In controlled studies, y is the number of deaths in the exposed and x is the number of deaths in the control cohort. Let $z=x+y$ be the total deaths.

The usual statistical measure of the health effect of the workplace or environmental change would be the relative risk of death (y/x). Let the observed or sample value of the relative risk be RR and the true value be T. Hence, if $T=1$ the site or workplace would be safe, or as safe as it was originally. If there is hazard, T will be greater than 1. For example, a doubled risk would be given by $T=2$.

Let A denote some "acceptable" relative risk, greater than 1.0, that would be permitted to declare an environment safe. There is general agreement that A should be about 1.10, indicating a 10 percent increase in deaths among the exposed. The choice of A is a societal and legal one; the value 1.10 is, according to Bross, founded in tort law and established scientific practice.

A standard statistical method to control false positives is to use the estimator RR to set a 95 percent confidence interval for the parameter T. With this method, we can be 95 percent sure that T lies in a specified range. If L is lower limit of this interval and U is the upper limit, we can be 95 percent confident that $L<T<U$.

To demonstrate safety, we would want to argue that it is very unlikely that the true relative risk is greater than the acceptable relative risk A. In these terms, safety would be (statistically) proved if $L<T<U<A$.

To demonstrate hazard, we would want to argue that it is very likely that the true relative risk is greater than the acceptable relative risk A. In these terms, hazard would be (statistically) proved if $A<L<T<U$.

The minimal statistical requirement for a valid proof of safety is that the square root of z, sqrt(z), be at least as large as the right hand side of equation (1).

$$\text{sqrt}(z)=(RR+1)(A+1)/(A-RR),\quad RR<A, \qquad (1)$$

while the corresponding requirement for a valid proof of hazard is that sqrt(z) be at least as large as the right hand side of equation (2).

$$\text{sqrt}(z)=(RR+1)(A+1)/(RR-A),\quad RR>A. \qquad (2)$$

The two requirements are symmetric. The requirement that RR be less than A for the application of the requirement for safety agrees with common sense in that one would not be interested in proving safety when the observed relative risk was greater than the acceptable relative risk. Similarly, one would not want to prove hazard when the observed relative risk was less than the acceptable value.

While the value of RR depends on the particular study, we can get an idea of the order of the magnitude of z by using the numerical value of T as a surrogate for RR in these equations. Substituting A = 1.10 and RR = 1.0 in (1) gives sqrt(z) = 42, or z = 1764. Thus, if the observed relative risk were 1.0, one would require at least 1764 deaths to be 95 percent confident that the true relative risk is less than the acceptable relative risk A. Substituting A = 1.10 AND RR = 2.0 in (2) gives sqrt(z) = 7 or z = 49. Hence, if RR = 2 one would require at least 49 deaths to be 95 percent confident that the true relative risk exceeds the acceptable relative risk A.

An appreciation of the sample sizes required to produce 1764 deaths can be gained from data derived from the AFHS. In the soon to be released 1989 mortality update, the overall cumulative death rate in both Ranch Hands and Comparisons combined was about 2.8 deaths per 1000 person-years. The observed overall relative risk, RR, was 1.0. Suppose one wanted to design a new study of these populations to demonstrate safety. Bross's minimal requirement is 1764 total deaths with RR = 1.0 and A = 1.1. Let N denote the total person-years of follow-up required to yield 1764 deaths in both groups. We would then have 2.8*N/1000 = 1764 or N = 571,428 person-years of follow-up and, in a study with equal group sizes, 571,428/2 = 285,714 person-years of follow-up per group. Since the average time since Vietnam exposure is 17 years, the resultant minimal sample size per group would be 285,714/17 = 16,806. Thus to make assurances of safety with 95 percent confidence, having observed RR = 1.0, we would require at least 16,806 Ranch Hands and an equal number of Comparison subjects. This is an impossibility since there are only 1261 Ranch Hands.

The sample size requirement for demonstration of hazard is far less severe, as can be seen by repeating the previous example with z = 49, assuming RR = 2 was of interest. In that case the minimal requirement is 515 subjects per group, which is, of course, exceeded in the AFHS. Thus, the AFHS is large enough to prove hazard, but not large enough to prove safety.

EXPOSURE MISCLASSIFICATION AND ITS CONSEQUENCES

In the absence of dosimetric data, epidemiologic investigators have generally used work history information to index exposure. For example, in a mortality study of male workers in a Montana smelter, Lee and Fraumeni (11) used the number of years worked in moderate and heavy arsenic areas to index exposure. Similar indices have been used in studies of asbestos and chemical exposures. Such indices, although crude because they ignore individual variation and work habits, can suffice to demonstrate a dose response effect, as was the case with Lee and Fraumeni and many other studies of occupational exposures to toxic substances and chemicals.

Following these and other examples, the Air Force Health Study indexed Ranch Hand exposure to TCDD by E, given by E=C*G/P, where C was the concentration of TCDD in the herbicides sprayed during an individual Ranch Hand's tour, G was the total number of gallons of herbicide sprayed during the subject's tour and P was the number of personnel in the subject's job specialty at his base during his tour. This index was prescribed in the study Protocol as the best available index, given available data. Self-reported exposures have been avoided to preclude the possibility of reporting bias.

An assessment of the validity of E as a measure of TCDD exposure has recently become possible since the development of the serum TCDD assay at the CDC. The ongoing CDC assay of AFHS participants allowed a display of the relationship between E and current TCDD body burden. Additionally, the half-life estimate together with known times since tour and the assumption of exponential decay permits a study of the relationship between E and the estimated initial Ranch Hand TCDD dose.

The assay results indicate that, as a group, the Ranch Hands have been significantly exposed to TCDD and that, as a group, the Comparisons are unexposed. All but two of 352 assayed Comparisons have a current TCDD body burden less than 15 parts per trillion (ppt), levels that are considered background trace amounts; the Comparison mean is 4.7 ppt. In contrast, 51.6 percent of 374 assayed Ranch Hands have current values above 15 ppt; the Ranch Hand mean is 32.2 ppt. If the threshold for background exposure is taken as 10 ppt, as suggested by this and the CDC ground troop study (12), 68.2 percent of Ranch Hands and 2.8 percent of assayed Comparisons have current TCDD levels above background.

However, a plot of E versus current TCDD body burden in the 374 assayed Ranch Hands shows no association; correlation=-0.03. Further, no association is seen between E and extrapolated Vietnam TCDD dose, correlation = 0.02, or between the logarithms of these quantities. These results will be described in detail when all Ranch Hands have been assayed. The lack of association between E and current TCDD body burden may be due to the short duration of exposure, about one-year for most Ranch Hands, and variation in individual work habits and duty. These aspects are currently under investigation.

The TCDD assay results so far indicate that E is not a valid measure of current or extrapolated initial TCDD body burden in Ranch Hands, diminishing the validity of all previous attempts to detect a dose response relationship with E. The entire study will be reanalyzed with the TCDD assay results, and the extrapolated Vietnam TCDD dose, as the indicators of exposure. This reanalysis is scheduled to begin in September 1989. The results will be released at the conclusion of a one-year analysis and report writing period, in the fall of 1990.

About 48 percent of assayed Ranch Hands have current TCDD levels below 15 ppt, a level that may be regarded as an upper limit for background exposure. Without additional data, we can only assume that these Ranch Hands were not exposed in Vietnam or that, in the worst case, they were exposed and their body burdens have decayed to background levels. The reanalysis of study data will take both possibilities into account. If they were, in fact, not significantly exposed in Vietnam, current estimates of relative risk in the AFHS are biased toward finding no effect.

The magnitude of the bias due to misclassifying exposed subjects can be assessed in terms of the bias of estimated odds ratio, a quantity sometimes estimated by statisticians instead of the relative risk. The odds ratio approximates the relative risk for rare diseases. In the case that only about 60 percent of the Ranch Hands were significantly exposed to TCDD in Vietnam, if the true odds ratio or relative risk were 2, one would estimate an odds ratio of about 1.1 and thus miss finding the health effect, assuming 1000 subjects in each group, a disease prevalence of 5 percent in the Comparison group and an exposure prevalence of 2 percent. If the true effect were a tripling of disease prevalence, an odds ratio or relative risk of 3, the estimated value would be about 1.2. Thus, with misclassification as high as 40 percent, a doubling or tripling of disease prevalence could be missed in a study as large as the AFHS. These bias estimates and their consequences are being avoided in the AFHS via the introduction of assay results as the exposure index.

CONCLUSION

In the context of occupational exposures to advanced composites, epidemiologic studies are statistical investigations of health effects in human beings that can complement animal experiments in the resolution of health complaints. The prospective Air Force Health Study has been discussed as an exemplary study of health effects in a cohort occupationally exposed to herbicides and their contaminant (TCDD).

The interpretation of the many statistical associations that can arise in an epidemiologic study requires careful consideration of the multiple testing artifact and established causal criteria. In studies with many endpoints, such as the AFHS, interpretation is challenging and not always conclusive due to conflicting prior knowledge and unknown latency periods.

Bross's (8) calculations show that epidemiologic studies designed to demonstrate safety are, in practice, not feasible. Further, an observed relative risk of 1.0 in a study designed to detect hazard is not a valid basis for assurances of safety.

Work history indices of exposure, while sufficient to detect a dose response effect in past studies of occupational exposures to toxic chemicals, are subject to error when the exposure is weak or the period of exposure is short. Additionally, exposures can be highly heterogeneous, as was TCDD exposure among Ranch Hands, and this can lead to a strong bias toward finding no effect.

This discussion has been centered around the prospective AFHS as the example. Case-control studies focused on a single disease endpoint and a single exposure are less prone to the multiple testing artifact, but still subject to issues of exposure index error. Bross's calculations apply to case-control studies as well as to prospective studies.

REFERENCES

1. Lathrop GD, Wolfe WH, Albanese RA and Moynahan PM: Epidemiologic Investigation of Health Effects in Air Force Personnel Following Exposure to Herbicides: Study Protocol. 1982, NTIS AD A 122 250.

2. Lathrop GD, Wolfe WH, Albanese RA and Moynahan PM: Epidemiologic Investigation of Health Effects in Air Force Personnel Following Exposure to Herbicides: Baseline Morbidity Study Results. 1984, NTIS AD A 138 340

3. Lathrop GD, Machado S, Grubbs W, Karrison T, Wolfe WH, Michalek JE, Peterson MR and Miner JC: Epidemiologic Investigation of Health Effects in Air Force Personnel Following Exposure to Herbicides: First Follow-up Examination Results. 1982, NTIS AD A 188 262.

4. Patterson DG Jr, Needham LL, Pirkle JL, et al: Correlation between serum and adipose tissue levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin in 50 persons from Missouri. 1988, Arch Environ Contam Toxicol 17:139-43.

5. Wolfe WH, Michalek JE, Miner JC, Peterson MR, Patterson DG, Needham LL and Pirkle JL: Serum 2,3,7,8-tetrachlorodibenzo-p-dioxin levels in Air Force Health Study Participants - preliminary report. 1988, MMWR 37:309-11.

6. Pirkle JL, Wolfe WH, Patterson DG Jr, Needham LL, Michalek JE, Miner JC and Peterson MR: Estimation of half life of 2,3,7,8-tetrachlorodibenzo-p-dioxin in Vietnam veterans of Project Ranch Hand. (In press).

7. Kleinbaum DG, Kupper LL and Morgenstern H: Epidemiological Research: Principles and Quantitative Methods. 1982. Lifetime Learning Publications. Belmont, California.

8. Bross ID: Why proof of safety is much more difficult than proof of hazard. 1985, Biometrics 41: 785-93.

9. U.S. Environmental Protection Agency: Environmental monitoring at Love Canal. 1982, Vol 1. Washington DC, U.S. Government Printing Office.

10. Millard, SP: Proof of safety versus proof of hazard. 1987, Biometrics 43: 719-725.

11. Lee AM and Fraumeni JF Jr: Arsenic and respiratory cancer in man: an occupational study. 1969, Journal of the National Cancer Institute 42:1045-1052.

12 Centers for Disease Control: Serum dioxin in Vietnam-era veterans - preliminary report. 1987, MMWR 36:470-5.

MSDS Adequacy/Availability

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ABSTRACT

Since they were originally required by OSHA under their shipyard standards 29CFR1915, 1916, and 1917 released in the early 1970's, Material Safety Data Sheets (MSDS) have become a cornerstone of Industrial Hygiene and Chemical Safety programs. Despite the narrow focus of the regulations requiring an MSDS they became the defacto standard format for conveying health and safety data from suppliers and manufacturers to their customers.

The growth in the use of MSDSs has raised many concerns about their availability and adequacy. Initially MSDSs were generally not available because requirements for their preparation did not have the force of law behind them in the majority of industry. Later with inclusion of requirements under Hazard Communication Standards they became more plentiful but specific data sheets are still not always available.

There are many possible reasons for difficulties in obtaining an MSDS. Preparation requires a dedication of resources to search out needed information. There may still be companies which are not consistently willing to commit to this requirement and prepare an MSDS prior to processing or replacing materials for distribution. A problem may also develop where a supplier is the sole source of a material. The alternative of changing supplies to get needed information does not exist. This, however, is significantly less of a problem than in the past.

Of greater concern is the issue of the adequacy of information provided by an MSDS Adequacy actually encompasses two areas. They are the accuracy of the information that the suppliers provide and the sufficiency of that data.

The volume of chemicals used by most companies requires them to accept information presented in Material Safety Data Sheets at face value. This is of critical concern where significant deficiencies exist. Proper preparation of an MSDS requires familiarity with toxicological principles and references. In addition, while the law does not require it, the ability to conduct toxicity testing is a definite advantage in conveying hazard information

A large manufacturer is able to retain a sufficient staff to evaluate their products and develop detailed MSDSs. This is not true of smaller suppliers whose best efforts can fall short. The inability to review data for technical merit before inclusion coupled with insufficient time to properly review all references can lead to a deficient MSDS.

There is also the problem of the limited requirements for providing information on MSDSs. OSHA requires only a search of available literature before preparing an MSDS. This is a particular problem for materials where little information has been developed by toxicological evaluation. These products include the vast majority of chemicals in the marketplace.

In general the utility of MSDSs could be significantly improved if the areas covered and technical references could be expanded. Access to specific disposal information, personal protective equipment guides, and interactive effects data would greatly enhance employee and environmental protection.

PRESENTATION

The first MSDSs were produced in the early 1970's as part of OSHA's shipyard standards. They were part of an innovative concept requiring manufacturers to supply customers with detailed safety information about the products they purchased. These forms were found to be so useful that customers outside the shipyards requested them. Suppliers began to prepare them because of industry demand, not regulation.

In the 1980's some other regulations came into existence. EPA's superfund amendments (SARA), and more specifically, SARA Title 3, requiring specific actions based on material safety data sheets. MSDSs were also required by the OSHA Hazard Communications Standards, which modified the original data sheet form, but did not make the new form mandatory. Substantially similar forms are acceptable, which sometimes creates problems. It is often difficult to locate information quickly when placement varies from a standard.

The Hazard Communication Standard also places a burden on the user of materials. The regulatory and the financial burdens involve people who are using products along with manufacturers. For example, employees may have the right to refuse to work under specific circumstances if material safety data sheets are not available within a given time period

This regulatory mandate makes any concerns regarding MSDS availability even more significant. It is particularly significant when dealing with newer technologies like composites where safety information is rapidly changing. Maintaining current material safety data sheets for such products can be very difficult. When problems are encountered with employee concerns regarding products, there is a heightened need for awareness of ingredients and associated hazards. In order to fill this need there are some very significant issues affecting users which must be addressed.

For the user there is a need for administrative controls, the actual gathering of the material safety data sheets. This may seem simple, but when you are dealing with the industrial environment, materials don't always come into the facility in a very orderly manner. This is particularly true when you are in research and development phases of operations as is often the case with composites. Products may come in through the normal purchase order procedure, as samples or from other sources. In many cases the material safety data sheet may not accompany these "test samples". Strong purchasing controls are essential. The need to have control over what comes into your facility is critical whenever you work with potentially hazardous chemicals. MSDSs are the best method of obtaining safety information available at the present time.

There is another issue relating to the MSDS format. Some suppliers provide ten-page MSDSs while others do not completely fill out the basic two. Finding information on the material safety data sheet can require some effort. They are sometimes cloaked in trade secret, legalistic terms to protect the supplier. Quite often any deficiencies must be corrected by the user after extensive investigative research. There has been some testimony before Congress in the recent past relating to the Hazard Communication Standards, which addresses this issue directly. Much of the burden for comprehensive review has shifted to the user of materials, which is not where it belongs. Companies occasionally have to reverse engineer the products that they receive in order to ensure that all hazards are identified.

There is also an issue related to sole-source materials. Sometimes a product has only one supplier and is required by contract. In this situation little pressure can be exerted on a supplier to provide comprehensive safety information. The user's ability to force the manufacturer to provide a complete MSDS is limited. Patented, state-of-the-art materials where the toxicology has not been completely developed can exacerbate this problem.

The other major issue regarding MSDSs is their adequacy. While material safety data sheets are becoming more available, quality is still an issue. There are some common deficiencies. Anyone familiar with material safety data sheets is aware that they are divided into sections prepared by various disciplines. Unfortunately a shift in responsibility for preparation from toxicological, safety, and health professionals to legal professionals often occurs. This protection against lawsuits often affects what is put on a material safety data sheet. For example, with regard to personal protective equipment, the maximum level is often recommended. Working with a common solvent, the personal protective equipment section may recommend self-contained breathing apparatus. This is excessive for normal operations and most companies could not justify such equipment based on employee risks but suppliers assume worst case scenarios.

With regard to hazard determination, the law requires only a review of available literature. A fraction of the chemicals in the marketplace has been analyzed in depth, and even for those there is quite often conflicting information available. It is an art to determine which study has more value. There is also very little information available regarding synergistic effects that occur when products are used in combination. Even for composites where they are intended to be mixed together, such data has not been developed.

Large suppliers often have groups of employees dedicated to preparing material safety data sheets. This is not always true for smaller suppliers. This variability in available resources affects MSDS quality. The technical expertise of individuals assigned MSDS preparation responsibility may not encompass the full scope of knowledge that a material safety data sheet requires.

The preparation of data sheets requires familiarity with references. Those required to be reviewed are listed in the regulations. However, just knowing what the books are is not the key to understanding and being able to convey that information to users. They are technical references and the nomenclature is very difficult, as is the required translation to layman's terms. Knowledge of toxicology is essential and is often not present. Without such knowledge rote transfer of information from references onto data sheets is not always accurate or helpful to the user.

Real improvements are needed in material safety data sheets. The practicality of accomplishing these changes is dependent upon the information that is available and a supplier's ability to conduct required testing. This does not refer to legal requirements because very little testing is required by regulation. It is, however, suggested by good

business practice. Studies are expensive. Few companies can spend the hundreds of thousands of dollars that may be required to test each of their products in a comprehensive fashion.

Additionally, the data base available needs to be improved and refined in a very formal manner. For companies that may not have the particular expertise required, there needs to be a compilation of information to place on material safety data sheets. There is a growing desire by purchasers for uniform material safety data sheets. The issue of variability between suppliers is very real and can lead users to switch from one manufacturer to another in order to get the better data sheets. These are documents that employees use, and quality counts.

Finally, trade secrets deserve mention. This has been used in a protective posture in the past. It's a less frequent choice today, because of some very stringent regulations and the definition of what can be classified as a trade secret. To qualify as a trade secret, mixtures cannot have been previously disclosed, be required by federal law, or be readily discoverable by reverse engineering. There are very few products immune from these exceptions. These are good regulations because, while trade secrets are important, and certainly an essential element of any business, in the area of safety and health secrets can be hazardous.

Industry needs to convey to employees what potential danger they face and what precautions they require in order to work with materials they are given. With an effort towards preparing information that is both usable for industry and easily prepared by manufacturers, we can substantially improve our posture in protecting the safety and health of all employees.

HAZARD COMMUNICATION AND COMPOSITES

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ABSTRACT

The OSHA Hazard Communication Standard includes several basic requirements which apply to composites just like any other chemical product. The manufacturer is responsible for product evaluation, providing a Material Safety Data Sheet (MSDS), and labeling. The employer using the product must ensure that the product is properly labeled, make the MSDS available to the employees, and train them on the hazards of the product.

Particularly with new composite materials, general employee training and the availability of MSDSs is not enough. A good practice is the preparation of a product handling requirement sheet giving specific information on using a particular composite at their facility. This handling guide can be attached to the MSDS and should provide specific information on work procedures, engineering controls to use, and personal protective equipment for each stage of the composite part fabrication.

Another good practice is to communicate in an atmosphere of openness with the composite workers. There should be a name and phone number on the product handling sheet so concerns or further questions can be directed to the right person. Listen to their concerns. Answer their questions.

If the facilities, engineering controls and personal protective equipment are not adequate, push for what is needed. Involve the workers in suggesting better ways to work with the materials. Equipment does exist to minimize personnel exposure by inhalation and skin contact, although it may need to be modified for composite areas. Instruction on how and when to use this equipment is part of a good hazard communication program.

PRESENTATION

The OSHA Hazard Communication Standard applies to composite materials just like any other chemical material. The composite manufacturer must evaluate his product and provide this information to the purchaser in the form of an MSDS. Manufacturers are required to provide certain information on the MSDS to enable the user to work with the product safely.

The purchaser or employer must provide this information to employees potentially exposed to the product.

In addition to providing the MSDS information, the employer must have a written program describing the methods used to comply with the Hazard Communication Standard at that facility, must ensure that all chemical materials are properly labeled, and must train the employees.

Training must include the potential hazards of the materials, the safe handling procedures, how to detect hazardous conditions, and a plan to follow in case of an emergency. We are going to look at the first two with respect to composites; training and safe handling procedures. How you conduct your training determines how successful it is. The material needs to be relevant to the group being taught.

The instructor should want to be there, should be familiar with the work, and have a caring attitude. Visit the area before the training. See what they work with. Ask questions. Find out what chemical concerns them the most. Use that MSDS in your presentation. Small training classes are good - 20 is a good number. It's best if they all work with the same types of materials.

If using video, do not let the video last more than 15 minutes at a stretch. Intersperse with discussion, questions or relating the information to your facility.

Answer their questions. If you don't know the answer, get back with them later. Give them your name, phone number and shift. They may have questions later.

Particularly with new composite materials, general employee training on composite materials and availability of MSDSs are not enough. A good practice is for the safety and health professional at the using facility to carefully evaluate the formulation of each new composite material and write a very specific Product Handling Requirements Sheet. This should provide specific information on using that composite at their facility. It should include work procedures, engineering controls, and personal protective equipment for each stage of composite part fabrication.

Most important is that the worker is given this sheet attached to the MSDS prior to beginning work on the new material.

Sources for this additional information are the composite manufacturer, other companies who have used that material, and reference literature. It used to be a challenge to locate someone who could discuss the formulation. It's getting much better. If you have access to a lab, testing can be done to determine the off gassing products of the composite

at the temperature you may have to use in shaping. This helps in determining what kind of ventilation and personal protective equipment will be necessary.

When developing these handling guides, it is necessary to think of the entire process of composite use, from rolls of new material to the finished part.

Headings on the product handling sheet should be written for the worker in short, simple sentences.

First, include the product name, manufacturer, date, and product description. This should include appearance, type of resin system and fiber, and information on the effects of skin exposure (is it carcinogenic, by what route of entry, etc.).

Second, there are special handling procedures. Should you avoid direct skin contact? What about inhalation of fibers? Can the material be heated in open shop areas? Is there a temperature which should not be exceeded based on off gassing products? During the cure cycle, should autoclave and vacuum lines be exhausted through a cold trap? How and where should trimming, drilling, routing, and grinding be done?

Personal protective equipment is divided into sections on the uncured and the cured material. Uncured material: Should gloves be worn? Specify which type. Is forearm contact likely? Wear sleeves. How about leaning over a large part? Dermatitis can occur in the midriff area from leaning over a large part. Cured material: When generating dust from finishing the cured material, what personal protective equipment should be worn? Which respirator? What clothing to keep dust off the employee's skin and clothing? What dust collection method? Some jobs can be machined wet.

Additional information: Refer them to the specific MSDS for the product. The most important part of the handling guide is the preparer's name and phone number to contact if there are questions or concerns.

Remember, we are talking about communication. It is a two-way street. An atmosphere of openness is extremely important.

Another good practice is to check back with the using group, preferably in person, to see how the recommended practices are working. You will probably learn something new. Listen to the workers' concerns. If you cannot answer their questions, find the answer and get back with them. If you need to revise your Product Handling Sheet, do it.

If the composite facilities are not adequate, if the right equipment for engineering control of the hazards is not available, or if the personal protective equipment is not stocked, work to get what is needed.

A good source of ideas on better ways to work with materials is the workers themselves. Even if you cannot incorporate their ideas, your changes will be better accepted if they have had a chance to participate. There is a lot of talent out there in blue collars. Also, contact other composite-using companies. Often the supplier can tell you which other companies are using the material. They may have some good ideas.

Equipment does exist to minimize personnel exposure to the dusts and vapors as well as to reduce skin contact, although it may need to be modified for composite areas.

If you have an MSDS computer system, the fact that a product handling sheet exists can be noted in the system. However, it is better if a paper copy of the handling sheet with the attached MSDS is handed to the employee using a new material for the first time. If the workers in the test part fabrication facility are instructed to not begin work with a new material until they have seen the MSDS and product handling sheet, and if everyone involved understands the system, it will work smoothly. Workers like it - they know someone has looked carefully at the material - someone cares about them! Supervisors like it because work progresses smoothly without shut downs. Engineers like it because they get their parts made. And, the safety and health professionals now know what new materials are coming into the facility and will have an opportunity to provide safe handling procedures.

What has actually happened is that the engineer planning the part learns that he must obtain an MSDS and get it to the safety and health professional with enough lead time for the evaluation to be done. I cannot recommend this system enough. After awhile, a good collection of product handling requirements sheets is developed. If it goes into production, you have a guide.

Here are some ideas that have been tried to minimize employee exposures. A typical composite area requires good general room ventilation. Some are temperature and humidity controlled to slow the curing process.

Automated cutters may be mechanical or laser type. This cutting table surface is totally porous with down draft exhaust ventilation. With new rolls, volatile vapors can build up inside the plastic, especially bismaleimide materials. By poking a hole in the bag and inserting a vacuum line for a few seconds, the vapor can be pulled out. Check first to see where the vacuum line exhausts. In this area, by keeping paper or plastic over the material, hand contact can be minimized.

In a crude attempt to make a local exhaust hood over a lay up room table, a slot was cut along the back edge of the table and connected to the duct work below. It works quite

well but is an area for equipment design people to work on. The hood was made for cutting and lay up of a very dusty prepreg with an aminobiphenyl component.

Cut composite material being shaped over a mold involves a lot of hand work in making the rather stiff and bulky material curve smoothly.

Irons are used to heat small areas at a time to make the composite lay smoothly. For concave surfaces, by heating only a small area at a time, off gassing of volatiles is minimized. The fabric over the prepreg keeps the iron clean and, if cut large enough, reduces hand contact. The iron is modified to prevent high heat.

Heat guns are also used to heat small areas. Heat guns have been altered to control the maximum heat generated and seem to dissipate the off gassing products.

Basic rule for working with uncured composites: avoid skin contact and wear gloves, sleeves, and apron or coat. Hands, wrists, and midriff are most common sites of dermatitis from uncured composite work.

Parts are put into autoclaves for curing. It is a good idea to have a cold trap for vacuum lines. The atmosphere inside autoclave during curing is often nitrogen. Potential for oxygen deficiency exists if the autoclave is entered too quickly. If an inert atmosphere is made from natural gas, carbon monoxide and nitrogen oxides can occur in high concentrations.

Down draft tables with hoods for small jobs may experience problems with filters which can fill quickly with dust. The changing of filters is a continuous maintenance problem Dust collection systems are better and should be designed for ease of cleaning.

Gloves and sleeves are helpful in keeping dust off skin. In a booth, a vacuum cleaner may still be needed to collect large particles that stay on top of the part. Some booths may have a dust collection system with a self-cleaning shaker.

Robots can be used for repetitive part trimming in conjunction with a dust collection system which has particle size separators and system of filters. The filtered air goes back into the room.

The molds or tools need to be cleaned before reuse. Hand scraping of residue and solvent cleaning are the old ways. The cryoblast shoots carbon dioxide pellets at the tool. The residue freezes and comes off. This system contributes to an overall solvent usage reduction. If the area is not well-ventilated, high carbon dioxide levels can become a problem before there is a low oxygen level.

Glove selection for composite work is a real challenge. One group used this criteria to find an adequate glove. Basically, the employee needed a glove he could work with, it had to provide protection, and it could not cause delaminations in the finished part. (Criteria were: high finger dexterity, ability "to feel the ply" through the glove, resistance to typical resin system components when contacted in the "B" stage, length to cover wrists and overlap sleeves, comfortable to wear for long periods of time with minimum perspiration generated, sized for men and women, removable without turning inside out, and must not interfere with the bonding of prepreg materials.)

It has been a three-year project. Prior to that, barrier creams, heavy latex surgical gloves, and cotton lisle gloves have been worn. Gloves were tested for silicone, hydrocarbons and anything else which could be identified that might interfere with prepreg bonding. Many gloves had a high silicone level on the surface. Testing procedures need to be conducted very carefully as common items (like plastic bags and food grade aluminum foil) have a lot of silicone on the surface.

A glove has been developed which is specifically manufactured to have low silicone levels on the surface. It is a cotton lisle-lined latex glove, which would not be the glove material of choice based on chemical resistant glove permeation data. However, it seems to be an effective barrier "in the field". And, the latex glove can be manufactured with low silicone and hydrocarbons on the surface. Most workers like it. The glove is not expensive, and we are monitoring closely for part quality.

It would be good to have more than one glove, particularly one that would "slide" along on the prepreg material to shape the prepreg material around curves. We all need to share this kind of information.

I have some recommendations for improving the MSDSs we receive from the composite manufacturers. They may wish to ask their suppliers the same questions.

1) Include the name and phone number of the person or department to call for additional information. It can take a long time to find the right person. Sometimes the phone number given is not even in the same part of the country. If you find the right person, save the name and phone number. It will make it easier to ask a question next time.

2) The more we know about a composite formulation, the better we are able to work with it safely. We cannot make good choices on substituting for a less toxic formulation if we do not know the exact components. Also, CAS numbers, the only specific, widely accepted chemical identifier, should be included for each component material.

It takes a great deal of time and money to test a product to qualify it for our use. Our customer must approve all changes. When making a substitution for health reasons, we want to be very sure that we are actually making a significant improvement from a toxicological standpoint. To substitute with a closely related chemical, one which is just not yet regulated, but which has the same toxicological effect, is not advantageous.

Those safety and health professionals who know proprietary components must be very careful to protect that information from other resin system or prepreg formulators.

3) One more section on an MSDS would be very helpful to prepreg users. The uncured composite will probably be heated during the lay up process. Tell the users what off gasses at 120°F, and give the approximate parts per million airborne level expected at 1 foot from the heated prepreg. It will help both the suppliers and the users know what is going on in the mixture. The worker's potential exposure can be determined ahead of time. Eventually, the levels of those common off gassing products that will be irritating to the eyes or respiratory tract will be known.

Our choice, of course, would be to use prepreg materials that can be heated to 120°F without the necessity of a lab hood or a full face respirator.

We have tried some of this air sampling. We get very low levels; many of the off gassing products are complex organic molecules and are found in parts per billion levels. But, the levels of these organics which cause irritation are not in the literature. By doing this testing, we would develop data to indicate the levels which can be tolerated without eye irritation, etc.

This testing would have to be a standardized procedure. We have tried Envirochem® tubes and charcoal tubes run at the same time to get both a wide range of organics plus some idea of the relative quantity. The charcoal is more precise, but the Envirochem® tube, which is thermally desorbed, picks up more compounds. We are working on developing a standard test procedure as a starting point for industry evaluation.

4) When composite prepreg formulation has proprietary components, it would be helpful to the safety and health group at the user facility if the resin system components were numbered. Proprietary ingredients would be listed as, "component 1", "component 2", etc. In the sections on health effects and toxicological data, the same numbering system would be used. This should not be that much of a problem for the formulator because he is receiving individual MSDSs from suppliers on each component. It might even make MSDS preparation easier. Some MSDSs have already been done this way.

> Because we are talking about communication, I think we would all agree that anyone of us providing hazard information, whether verbal or written, needs to be sure that the information is as accurate as possible. Deliberate misrepresentation, whether minimizing or exaggerating the hazard, is irresponsible. It can harm people either way.

A closing thought ... when choosing staff in safety and health or training areas, jobs where the person will be interfacing with workers, look for those candidates with "good people skills". The ability to communicate effectively with people at different levels is very important. And remember, part of communication is listening.

In summary, composite materials can be used safely. However, we need to continue to improve our knowledge, work practices, and equipment in composite areas. Instruction on how and when to use special techniques and equipment is a part of a good hazard communication program.

HAZARD COMMUNICATION - REGULATORY PERSPECTIVE

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ABSTRACT

The Hazard Communication Standard (HCS) is based on the simple premise that workers have both a need and a right to know the hazards of the chemicals they work with, as well as the measures they can use to protect themselves. Workers who have access to such information will be better able to take steps to protect themselves. Employers will be better able to design appropriate protective programs, and thus reduce employee exposures. As a result, the incidence of chemical source illnesses and injuries will decrease.

The regulator requirements which have been promulgated to accomplish this purpose will be described. Under the HCS, producers of chemicals are required to evaluate the hazards of their products, and prepare appropriate labels and material safety data sheets to convey those hazards as well as additional safety and health precautions. Users of chemicals are entitled to receive properly labeled containers and appropriate material safety data sheets when they purchase a hazardous chemical.

The HCS further requires all employers who have employees exposed to hazardous chemicals to prepare a written hazard communication program; label in-facility containers; obtain material safety data sheets and make them available to employees; and train employees to understand and use the available information.

PRESENTATION

What I was asked to discuss today are the regulatory requirements of the Hazard Communication Standard. I assume probably a lot of you are already familiar with them, so I'm just going to kind of cruise through this very rapidly so I can leave more time for questions. I'm basically going to focus on some areas that we think are particularly important, and some areas we think are problems in terms of interpretations related to implementing this standard.

The Hazard Communication Standard actually appears in the Code of Federal Regulations in six different places. It's identical in all those places, but we have to have different parts of the Code of Federal Regulations for different industries. General industry would cover manufacturing and those types of businesses which I assume would cover most of you.

We've been working on Hazard Communication for a long time. Sometimes people think that standards just come out of nowhere. They really don't. OSHA is not an agency known for the speed of its rulemaking process. When Congress passed the Occupational Safety and Health Act in 1970, they actually anticipated that we would have rules that would apprise employees of the hazards to which they're exposed. However, over the next 13, 14 years, what we found is that this is not a very easy issue to handle. Everybody agrees in the abstract that employees need information. When they have information, they can take steps to protect themselves. When employers have adequate information, they can design better protective programs. The ultimate aim of all this is to reduce chemical source illnesses and injuries, i.e., besides the fact that it provides employees with the right to know the information about the chemicals to which they're exposed. But there are a lot of difficult areas to deal with, such as the protection of trade secrets, the definition of chronic hazards. So it really took us a long time to come to grips with those problems. In 1983 we did publish, finally, a final rule for the manufacturing sector - that's anybody who makes anything, not just chemical manufacturing. We were sued right after that. The upshot of that suit was that we were told to expand it to cover all employees who are exposed to hazardous chemicals unless we can show that it's not feasible. We did that in 1987. The Standard does now cover all industries, although some of you may be familiar with the fact that some parts of it have been stayed, three provisions in particular, as well as all of its application to the construction industry. Last week that stay was lifted by the Supreme Court, so we are now in the process of publishing a Federal Register notice putting the entire Standard into effect. If any of you have been not implementing some parts of it because of that stay, the entire rule will be going into effect on March 17.

The Standard starts with a Purpose Section and, as I already mentioned, the real purpose is to reduce the incidence of chemical-source illnesses and injuries. But it does that through several other purposes. One is that every chemical is to be evaluated to determine its hazards That's the most comprehensive approach. Some of you may be in states that have "Right-to-Know" laws where they have a list of chemicals that are covered by the rule.

There is no list anywhere that includes every hazardous chemical. Even the very longest lists are far from being complete. When we were doing this rulemaking, we looked at the possibility, for example, of using the NIOSH Registry of Toxic Effects of Chemical Substances (RTECS) as our list of chemicals that would be covered by the rule. At that time there were about 65,000 chemicals on that list. Another list that was approximately the same size in number of chemicals was the EPA Toxic Substances Control Act Inventory. And it also had about 65,000. So, we thought that these lists must be pretty close to being all the chemicals that are out there. But when we compared them by CAS Number to see what the overlap was, we found the overlap was between 6,000 and 7,000 chemicals. So what that means is that there were over 50,000 chemicals on the NIOSH RTECS that weren't being made anywhere. And there are over 50,000 chemicals being made for which no data have been published anywhere in the literature. That doesn't mean that the manufacturers don't know that they're hazardous. It just means that the data have not been published. So in order to truly have a "Right-to-Know" Standard, we decided that the most comprehensive approach would be to say that employees have a right to know everything there is to know about a chemical. So everybody who produces a chemical or imports it is required to survey the literature, their own files, whatever information they have, and provide that information to their own employees and to downstream employees.

There was also another purpose, which was to establish uniform requirements for worker "Right-to-Know". There were a number of states which passed "Right-to-Know" laws before we did the Federal Standard, and a lot of the business people were concerned that they were having to deal with different lists of chemicals, different requirements for labels. This Standard establishes a national standard. The only people who can have a worker "Right-to-Know" standard that is specific to a state are those states that have what we call OSHA-approved state plans. That means they have an agreement with us to do everything in that state that we would do, and they have to have a standard that is at least as effective as the Federal Standard. If it's different, it cannot pose a burden on interstate commerce. So what you have right now is the Federal Standard that applies in about 25 states and then there are 25 states that have OSHA-approved state plans where the state is actually implementing the standard. Most of those have standards that are identical to the Federal Standard, but you will find a few states that have somewhat different requirements. For example, Maryland has a state plan, and they require training more frequently. That's permitted under the state plan approval system.

Chemical manufacturers and importers are required to assess the hazards of the chemicals they produce or import. This is what we call a downstream flow of information We decided it was most appropriate to have the people who were preparing or producing the chemical be the ones responsible for providing the information. They're the ones who are in the best position to know. But beyond that, all employers are required to provide information to their employees who are exposed to hazardous chemicals. And exposure under Hazard Communication includes potential exposure as well as actual exposure. And it's not related to exposure limits so you do not wait to do Hazard Communication until someone's exposed over an established exposure limit. Essentially, if the chemical is present in a form in which employees could be exposed, then its covered by Hazard Communication. We've estimated that it covers about 32 million workers in 3-1/2 million establishments. So, it's a very broad scope standard for OSHA.

The Scope and Applications Section puts some limitations on the rule in terms of chemicals that are covered, and it also provides limitations for certain types of work operations. For example, in laboratories or in operations where hazardous chemicals are handled only in sealed containers, such as a warehouse operation. You don't have to have a written hazard communication program, don't have to have a list of hazardous chemicals. You have to keep labels on containers If a data sheet comes with a container, you have to provide employees access to it. And employees have to be trained, with particular emphasis on what to do in case of a spill or leak. In laboratory operations it was limited because people feel that laboratories generally have professional employees who know what they are doing. We had some concerns about that, especially when you can read in the literature that some researchers try out their products on themselves and see what happens. But in any event, we do recognize there are some feasibility concerns in laboratories so we have this limited provision. In the sealed container situation, like warehouses, they have a lot of chemicals coming in and out but they're really only exposed if somebody damages the container in some way. So we felt a more limited coverage was appropriate there.

We also have exempted from the labeling requirements chemicals that are labeled in accordance with other federal agencies, such as pesticides labeled in accordance with EPA. That's more of concern to chemical manufacturers so they don't have to duplicate labeling.

There are some things that are totally exempt from the rule. Hazardous waste when regulated by EPA under the Resource Conservation Recovery Act, primarily because they already have requirements for manifests, labels, things like that, providing information to

employees. Tobacco or tobacco products, mainly because the hazard there is from consumer use, not from exposure in the workplace to those products Wood or wood products, meaning solid pieces of wood that might be flammable or combustible. However, we don't really want every desk that leaves the furniture factory to say flammable or combustible on a label. That does not include wood dust. So if you had shops where people are sanding or grinding wood, wood dust is covered by the rule and other things that are used with the wood would be covered. For example, formaldehyde in particle board would still be covered by the rule. Articles are exempted, this microphone would be an article. It may be made out of stainless steel, which has nickel and chromium in it, but it's in a form that nobody's going to be exposed to it. So once something is in that stage of manufacturing where nobody is going to be exposed to the hazardous chemicals it becomes an article exempt from the rule Food, drugs, cosmetics, or alcoholic beverages that are in a retail establishment packaged for sale to consumers are exempt So drug stores don't have to keep data sheets on these kinds of things. Food, drugs, cosmetics brought into the workplace for personal consumption by employees are exempt. So you don't have to have data sheets for rubbing alcohol in a first aid station, for example. Consumer products that are used in the same manner as normal consumer use, resulting in the same duration and frequency of exposure are exempt If you purchase window cleaner to clean the window every once in a while we're not really concerned about that. But if you have somebody who is using that window cleaner eight hours a day, that's his job, then we are concerned about that. And we also exempted drugs that are in solid final form for administration to a patient, tablets, capsules, things like that.

There is a very lengthy definition section, and we find that a lot of the questions we get could be answered if people would go back and look at the definitions I would point you in that direction if you have problems understanding anything The most important things in terms of the scope of the standard are that it covers all physical hazards, and these are very specifically defined in the rule, as well as all health hazards And health hazard is very broadly defined. It's anything from an irritant to a carcinogen If there is one toxicological study that indicates an adverse health effect, then that substance is a health hazard for purposes of hazard communication That's a much lower threshold for health hazard than we would use, for example, if we were setting a permissible exposure limit But again, this goes back to the concept of it being a "Right-to-Know" standard, that employees

have a right to know, for example, that there's one study that indicates that it is a carcinogen Perhaps there will be more data later, but at least they have a right to know it at this point.

Again, as I mentioned, the rule has a downstream flow of information. We have this process where chemical manufacturers and importers are required to do the evaluation. That means that if you're a user of a chemical, you're entitled to rely on the information that you get from your supplier. The approach is what we call performance-oriented. That means we don't tell people specifically how to do it. We just judge them by the outcome. In other words, we look at the label and the data sheet. If it has the right information on it then we don't really care if they looked at fifty studies or ten studies to get there as long as they have the right information on the label and the data sheet.

It's been an interesting process. People have been asking us for performance standards for many years and now that they have one I think they're sorry that it ever crossed their lips! It's much more difficult for people to comply with, and it's also much more difficult to enforce. If you have something that is very specific, and someone knows exactly what they have to do, it's much easier to comply. This way, you're dealing with a hazard evaluation process that is very general, and it's difficult for people to know just how far they have to go to be in compliance with the rule.

Although it is performance oriented, we have provided definitions of hazards, basic criteria for evaluation, and a list of possible reference sources. So any judgments we make would be made within the context of those parts of the Standard. And we have established what we've called a "floor" of hazardous chemicals, or chemicals that are to be considered hazardous in all situations, regardless of what the producer thinks of it. And these would be any substance that OSHA regulates, anything for which ACGIH has promulgated a TLV, and in the area of carcinogenicity, anything which the International Agency for Research on Cancer (IARC) or the National Toxicology Program have found to be a potential carcinogen That part of the scope is probably the most controversial because each time that IARC, for example, publishes a new monograph, that adds carcinogens to the scope of the Standard There are some people who are unhappy with some of the things that IARC has done. But again, going back to the "Right-to-Know" concept, IARC is a well-established, international, professional body and employees have a right to know that they have determined that something is a potential carcinogen.

Mixtures is another difficult area. Most people are exposed to mixtures, but most toxicological studies are done on individual chemical substances. So we have designed

what we consider to be a conservative approach to make sure that mixtures are adequately covered. If you've tested it as a whole, and there would be some cases where that's true, obviously that's the data which you would use. It's the best data on that particular mixture. If it hasn't been tested for physical hazards, then the person doing the evaluation can use whatever available scientific data they have to assess the physical hazards of the mixture. What that means is, if they've got a Class 1A flammable liquid, but it's only there in a concentration of two percent, and they can calculate that it's no longer flammable when it's in the mixture, that's fine. If it hasn't been tested for a health hazard, we don't allow that kind of judgment. We say that if it's there in concentrations of one percent or greater, 0.1 percent or greater for carcinogens, then the mixture is assumed to have the same hazards as the components. And we even have a back-up for that provision, saying that if it's there in concentrations smaller than that, but can still present a health hazard, it's still covered by the rule. So if you had something, for example, that was a strong sensitizer, like MDI or TDI, and it was present in concentrations of less than one percent, it would still present a health hazard to workers so it would still be covered even though it was present in concentrations of less than one percent.

And once all that's done, every employer who's covered by the rule has to have a hazard communication program, which is a written plan that describes how he's going to meet the requirements of the rule in his particular workplace It doesn't have to be lengthy or complicated. It's just basically a blueprint for how hazard communication is going to be implemented in that facility.

It has to include a list of the hazardous chemicals, and that list can be kept either by work areas or by the entire workplace, as long as whatever terminology is used on that list is also used on the label and on the data sheet so those things can be linked together It has to include the methods to inform employees of the hazards of non-routine tasks. So if you send somebody out to clean out a reactor vessel every once in awhile, you have to have that addressed in your program. And the hazards of chemicals in unlabeled pipes Pipes are not required to be labeled under the rule. On multi-employer work sites, more than one employer on a site, and those employers are generating hazards that are going to expose other employers' employees, then they have to have a way to exchange information about that hazardous material and whatever protective measures are appropriate. This is particularly significant on construction sites, where you have many employers working in the same areas and they are generating things to which other workers are exposed.

There are three ways to get the required information to workers: labels, Material Safety Data Sheets (MSDS), and training. And we consider all of these to be very important They're not independent. They all rely on each other and you need to have all three of them working to really be effective in terms of getting information to workers.

On the labels there are a couple of key definitions. I already mentioned the identity. That can be any chemical or common name, as long as it appears on the data sheet, the list, and the label. So if you wanted to call it Magic Mixture A or Code No. 123, that's fine as long as the worker has a way to link that to the MSDS for the product. It also has to include an appropriate hazard warning. That means any words, pictures, symbols, or combinations that convey the hazards of the chemicals in the container. And the hazards would be, for example, "flammability" or "causes lung damage".

A lot of people have misinterpreted this hazard warning statement to mean things like "harmful if inhaled". They consider that to be a hazard statement. That's not a hazard statement. It tells you what the route of entry is, not what the hazard is. Now when you're looking for a hazard warning you want what the hazard actually is, not a precautionary statement, which is not prohibited but is not required by the Standard.

Labels are required on every shipped container that leaves a manufacturers' or importers' workplace. It has to include an identity, appropriate hazard warnings, and the name and address of the responsible party. Labels are required on every in-plant container and again, have to include an identity and appropriate hazard warning. The only exceptions are pipes, as I mentioned earlier, portable containers for the immediate use of the employee, always under his control, solid metals, for example, steel beams that might not be an article because they're used in such a way downstream that they generate hazardous materials If they're sent repeatedly to the same person downstream then the upstream manufacturer only has to send the label once. And in some cases we do allow written alternatives to in-plant container labels. For example, if you had a number of reactor vessels in an area that all had similar contents and hazards you could placard the area or have a batch sheet rather than actually labeling each container.

The purpose of a label is to provide an immediate visual warning. It is not the sole source of information, it's not the most complete source of information. Basically, it's to remind the worker that he's had training, that he's supposed to realize that there's a hazardous chemical here, and that he knows there is an opportunity to get more information from the MSDS. One thing that we know about labels is the longer they are, the less likely it

is that anybody's going to read them and pay attention to them. So, when you're looking at labels within the workplace, that is something to keep in mind. You load these labels up with a lot of text , you're not going to get anybody paying attention to them.

MSDSs, on the other hand, are the detailed source of information on the chemical These should be everything you ever wanted to know about the chemical, some people say, and then some. Data sheets for each hazardous chemical are to be provided automatically by the chemical manufacturer and importer at the time of the first shipment and whenever they are updated. They have to update within three months of getting new and significant information about the health hazards.

We have specified what information is to be included on a data sheet but we have not specified a format. This again is the performance orientation. We do have what we call OSHA Form 174, which is non-mandatory and doesn't have to be used, although many people do use it.

Distributors have to ensure that data sheets are provided to other distributors and employers. So again there's this downstream flow of information. Retail distributors have to provide data sheets on request, and they have to notify commercial customers that a data sheet is available. And the most important provision is that employees must have ready access to data sheets.

We're at a point now where we've essentially pushed all these data sheets out the door. There are many data sheets, it's been estimated there are 70 million different data sheets in circulation. Obviously, that's multiple suppliers for the same product, but actually 70 million different data sheets And they're being used for a multitude of different purposes This is creating a lot of problems in terms of how well they communicate the information they are supposed to convey. People are loading them up with a lot of information, not really thinking about the purpose of that information. And this is something that we're getting very concerned about. Some of them are so complicated that nobody can really understand them. Some of them are so bad that they have no useful information on them. We're looking at some research in this area, thinking about the design of data sheets, about the type of jargon that you use on them in order to make them better in terms of communication I was just mentioning to someone that I found out very recently that if you print a data sheet in all capital letters, you reduce the comprehensibility by 30 to 40 percent. And a lot of computer generated data sheets these days are coming out that way If somebody looks at it, but they're turned off by it right away, then your aim to communicate to somebody is not

going to be met. If you use terminology like "lacrimation" instead of "tearing of the eyes", you've lost, again, half of your audience. One answer may be that we may have to look at formatting of data sheets and put the information for workers up front, and perhaps gear the language to an understandable level rather than using very technical language. The physical and chemical characteristics, and things that are more important to the professional people, can be put at the end of the data sheet to help ensure that the workers can access the information, and use it to their benefit, because that obviously is the point. So this is an area where there's a lot of work going on, and I think in the future we'll see some changes and some research being published on this. And perhaps, from our viewpoint, this may result in a change in the non-mandatory format so that we can get people geared to formatting it in a more accessible way. And perhaps we can make some suggestions on how to use the proper language for the different sections.

We think data sheets are very important. Some of them are very good, as I mentioned, but some of them really do need a lot of improvement. One thing that we suggest to people who are receiving data sheets, employers or users, that are not any good, is to send them back to your supplier. Tell them that you want a decent data sheet . And if they don't do it, the next step is to give it to OSHA, and we'll do it for you. A lot of employers don't want to do that, but that's the only way they'll ever get improved. We must go back to the source, and keep going after them, and make sure the information is there

The third means of communicating to workers is training, and for many people this is the most important part, although you really have to have the written information on the labels and data sheets in order to be able to do this adequately. I understand that you've already had a discussion about training, but just briefly, the requirements are that employees be trained prior to initial assignment to work with a hazardous chemical and whenever the hazard changes or a new hazard is introduced into the work area. A lot of people seem to be interpreting this as meaning every time you buy a chemical you have to retrain. That's not true. If you've done training on all the potential hazards under the Hazard Communication Standard, all of the categories of hazards, then you don't have to retrain when you introduce a new chemical. You do, of course, have to have the specific labels and data sheets available to the workers. And that training is to include the hazards of the chemicals as well as protective measures and the components of the program. In other words, you have to explain to people what a label is, what a data sheet is, what the information means, how they're supposed to react to it, how they can protect themselves

That's how the Standard is going to work, if people really know how to access that information.

On trade secrets, the specific chemical identity of a chemical has to be listed on the MSDS. The only exception is if it's a bona fide trade secret, which means it can be supported in a court of law. Then all other information has to be disclosed, and the data sheet has to indicate that a specific chemical identity is being withheld.

We have found that there are a lot of people who thought that they had trade secrets, and they really don't. To have a trade secret you have to have something that took you some effort to develop. It cannot be readily reverse engineered. So, if you're selling a 55-gallon drum of Magic Mixture A that's 99 percent toluene, and your trade secret is you don't want someone to know that they can buy it for a tenth of the price down the street, that's not a trade secret. And you will not be able to maintain that as a trade secret under the Standard. A trade secret normally would be something that would be a complicated mixture where there really is an ingredient that would be very difficult to sort out in reverse engineering unless you really knew it was that you were seeking. For example, there are some lubricating oils that are very complicated mixtures that might have trade secrets But frankly, there aren't too many of them.

We've spent a lot of time discussing this in the rulemaking process, and thought it was going to be a big problem, and what we've found is that we've just had a handful of citations. And all we can think is that enough people realized that they really didn't have trade secrets, that they are disclosing the information. We're not seeing that many data sheets now that have trade secret claims on them.

The Standard does require, even if you have a bona fide trade secret, that information be given up under certain conditions. If you have a medical emergency, where the specific chemical identity is needed by a treating physician or nurse, they are entitled to get it. You can ask them after the emergency is abated to sign a confidentiality agreement But it is their call as to whether or not the information is needed. And if somebody was to withhold trade secret identities in that type of emergency situation, they would be subject to a willful violation of the Standard, which has a penalty of up to $10,000.

In a non emergency type of situation, any type of health professional who is providing services to employees (it could be an industrial hygienist doing sampling, could be a physician doing treatment) is entitled to that information. They may have to sign a confidentiality agreement and substantiate that they need the information, but they are

entitled to get it. And this is a very important protection for workers, because it is very difficult to provide health services to workers if you don't know what the specific chemical identity is.

There is fairly limited recordkeeping under the rule. The written programs and the data sheets have to be kept current. However, under the Access to Employee Exposure and Medical Records Standard, which is 1910.20, if you don't have any other record of exposure, a data sheet would be considered a record of exposure and would have to be kept for 30 years. So, it's important that you're aware of the requirements of that standard as well as Hazard Communication.

And the effective dates for the non-manufacturing sector were that as of September of 1987, data sheets were supposed to be sent with the next shipment to non-manufacturing employers. And originally all employers were supposed to be in compliance by May 1988. Due to various court actions, it went into effect for everybody except construction the first of August 1988, and now will be going into effect for construction very soon.

HAZARD COMMUNICATION - WORKER PERSPECTIVE

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ABSTRACT

As the representative of thousands of workers in the railroad, chemical, and aerospace industries, the International Association of Machinists and Aerospace Workers (IAM) is not unfamiliar with the range of injuries and illnesses caused by exposure to workplace hazards. Over the years, thousands of IAM members have developed such job-related diseases as asbestosis, lung cancer, dermatitis, and neurological problems. The increased use of composites in the aerospace industry and the illnesses we are seeing among hundreds of workers at certain aerospace facilities, give us serious cause for concern Workers at some facilities have been allowed to work with new composite materials without adequate information and training and without adequate engineering controls and protective equipment. We believe that compliance with OSHA's Hazard Communication Standard is merely a starting point for employers to control employee exposures to composites. Additional steps must be taken to prevent injuries and illnesses from the use of these materials.

This presentation will attempt to answer the question of what workers want with regard to their safety and health on the job and what programs are needed to protect workers who handle composites.

PRESENTATION

I do appreciate being able to come and speak about the worker's perspective. I think it balances out some of the discussions we've heard all week. What I will attempt to do is talk a little bit about what workers want in terms of safety and health on the job and what they're looking for from the Hazard Communication Standard.

First, let me talk a little bit about the Machinists Union. As LtCol Bishop mentioned, within the name of the International Association of Machinists and Aerospace Workers is the word "aerospace." Obviously, the Union represents thousands of workers in the aerospace industry. They also represent railroad workers, chemical workers, and a whole variety of

folks out there in industry. Over the years there have been thousands of machinists members who have been stricken with occupational disease, so the Union is not unfamiliar with work-related problems. The Union is very concerned now because we have seen workers at some aerospace facilities who have been allowed to work with composites without adequate information and training and without adequate engineering controls, personal protective equipment, and those workers are developing health-related problems. The Union feels strongly that the Health Communication Standard is merely a starting point, and that additional steps need to be taken.

Now, let's talk about what exactly do workers want. Put very simply, workers want to be able to perform their jobs without getting sick. Specifically, workers who handle composites want the following: They want complete information on the toxicity of fibers, hardeners, and solvents with which they work. This means that Material Safety Data Sheets (MSDSs) should have results of toxicity studies in language that they can understand. We need to have study results be put on the MSDSs in very plain English. The MSDS should include information on both short-term and long-term effects. Also on the MSDS should be recommendations on the type and amount of ventilation that needs to be present when using these materials and the particular type of personal protective equipment that's needed. I'd like to stress that we do need direction on these MSDSs, as we've heard all morning, in terms of the type of personal protective equipment that needs to be worn Saying that personal protective equipment on an MSDS is needed, is just not enough. We need to know exactly what kinds of gloves, for example, need to be used In addition to receiving this information on MSDSs, workers want this information before they're required to work with the materials This sounds very basic, but we have some problems with this out there at some facilities. Workers are not getting this information beforehand. If suppliers do not have adequate toxicity information, (and we're finding that out this week that there really are some gaps in what we know) then these materials should either not be used before their hazards are well understood or else, (and this is the more realistic approach) full protective measures should be taken until we develop the information that's available We cannot afford to allow workers to work unprotected with these materials while suppliers and employers are researching their hazards. Contrary to what's been said in earlier presentations, particularly yesterday, some employers have not provided adequate information to workers before they've been required to work with these composite materials and this has really created some problems.

The second item that workers are interested in receiving is hazard-specific training. They want to know how to properly work with fibers and resins, before they are required to begin this type of work. Workers need to know how to handle these materials safely. Workers also want to be able to actively participate in designing the training programs. We had a very good presentation earlier from Pat from McDonnell Douglas about just how to design a training program. I think that was excellent. I think we just need to add to that, that workers should be able to participate in that training process, and in some cases, even do the training themselves for other workers once they've been trained. I believe Du Pont, for example, has several programs, not in composites, but I know part of their asbestos training programs is worker-taught and is very effective. Again workers need this training before they are required to work with these materials. We've heard earlier that in some worker groups that have been handling composites where workers have been symptomatic, that they had received training. We take exception to this. If there had been training done, there would be documentation that such training was done, and we have seen no documentation that training existed before symptoms developed.

The third item that workers are interested in is that they want materials to be properly labeled in the workplace. Workers should not have to try to guess what's in containers and that does unfortunately exist right now. While we understand that there is a secrecy issue, there's concern about classified information. We suggest that at least the basic hazards should be on these containers so that workers can immediately identify a product that may be a particular problem

The fourth thing that workers are interested in is, obviously, good engineering controls and adequate protective equipment. Ventilation systems should be installed prior to the use of new composites and not just after health problems have developed. The same goes for protective equipment. Also, workers want input into how controls are designed, particularly in the area of work practices. Workers want involvement in coming up with work practice solutions to some of the exposure problems that we're seeing.

Now these four items that I've discussed are pretty basic. Actually, they're what's required by the Hazard Communication Standard All workers are asking is that employers and suppliers follow and comply with the law. Now, beyond that, I mentioned in the beginning that are some additional steps we're interested in and I'd like to talk about that briefly We feel that the Hazard Communication Standard is just a starting point. There are some other changes that need to be put into place. One change is that we, the workers, feel

that there needs to be a change in philosophy. Workers want their complaints to be taken seriously. Workers feel that there has been an effort to trivialize their complaints, to classify their complaints as psychological disturbances, when no one has yet resolved whether their problems are truly physiological or immunological. Workers resent a psychological labeling as psychologically disturbed - they resent that very deeply. We feel strongly that since so many problems have developed at more than one facility, we question whether there is a psychological component to this or not. We feel that a lot of what is going on is definitely job-related. Because health professionals may not have sufficient sampling methodologies or the toxicological information that we need to characterize a job-related problem, should we really dismiss complaints and conclude that people are psychologically unstable? We think not. If workers were psychologically unstable, why are some employers now spending hundreds of thousands of dollars on ventilation equipment and responding in a way that involves true industrial hygiene solutions? Obviously, if employers really believed there were psychological problems, they would be investing or trying to solve the problem from that perspective We're not saying that there's not stress or anxiety among the people who work at some of these facilities - clearly there is. As was mentioned a couple of days ago, a lot of these workers work tremendous amounts of overtime. Also, workers who have filed complaints and are symptomatic, were initially downgraded, they were placed in jobs with lesser pay, they were given unpaid leaves of absences, some up to a year with no pay. Workers who have filed claims have had their claims denied for workers' compensation. They've received, in our opinion, some very bad treatment after sharing their symptoms and complaints with their employers. Being ill along with this type of poor treatment, I believe, would make any us here in this room have some degree of anxiety.

In addition to being taken seriously, workers want to see a change in philosophy in approach to chemical exposures in the workplace. Workers feel that employers should take a prudent approach to occupational exposures and new composite materials by installing complete engineering controls and personal protective equipment before problems are allowed to develop. Today I think we did hear some discussion that in a [illegible] of cases, this is being done. Industrial hygienists and medical professionals should be allowed to be involved with the development of some contract specs and engineering in the use of these materials to prevent problems before they start. Industrial hygienists (IHs) should be called on before a problem develops and should be heard. In some cases industrial hygienists are called on, they make their recommendations, and nobody seems to be listening. Then when workers

develop symptoms, they're called on again to try to solve the problem that could have been prevented. If health problems continue to be seen, workers do want to play a role in the evaluation of these complaints. Let workers be involved in selecting the doctors who evaluate their medical complaints. And let them be involved with proposing the solutions.

So in summary, let me just review what I'm saying very briefly here. Workers want four things, all of which are supposed to be provided by the Hazard Communication Standard. They want complete information on MSDSs, they want training, they want labeling, and they want engineering controls and work practices. And they want this all up front, before they're exposed to new composites. They also want a change in their employer's philosophy on occupational disease. They want their complaints to be taken seriously. They want safety and health professionals to be allowed to become involved in protecting them before materials are introduced into the workplace, rather than after. And they want to play a role in the evaluation of these types of materials in their workplace and in the evaluation of their complaints.

In closing, let me add that I hope that as health and safety professionals involved with composites we don't get bogged down with the technical issues before us, and so bogged down that we miss the big picture. The big picture is that workers are experiencing health problems now and they need to be protected before other new composites are introduced. We feel both suppliers and manufacturers have a legal and an ethical responsibility in preventing future health problems.

VIII. CLOSING REMARKS

Gary D. Vest

Deputy Assistant Secretary of the Air Force for
Environment, Safety, and Occupational Health, Washington, D.C.

The sessions have been long and there's been a tremendous amount of work done and you're still here so that's very good. In November, we set out to convene this conference of industry, labor, Department of Defense, and other federal agency representatives to address the occupational health aspects of advanced composite technology in the aerospace industry. Specifically, we wanted to address what was known and, possibly more importantly, what was not known about the health effects of using composites. We wanted to look at engineering controls and protective equipment and their effectiveness. We wanted to ask about the need for epidemiological studies and the health effects of composites. We wanted to address exposure standards. And we wanted to talk about the availability of health information to the worker in the form of training and hazard communication. A number of people said that was not only a tall order in such a short time, but an impossible order.

I'm terribly impressed by what you have accomplished in just several days. I believe that it is clear, at least it's clear to me, that the challenge that we're talking about is indeed manageable. It's something that we can really step up to. It's not mysterious as many of the uninformed would say. We really do know how to protect our workers, we simply have to do it. I have six overall observations. I've learned a great deal, and I just wanted to share these observations because as we were going through this conference I was advised I'll get to share some of my observations in the first congressional hearing on this topic which is scheduled for the sixth of March.

The first observation is that advanced composite technology is truly critical to the national interest. Not only in terms of defense systems, but to society in general

Second, the rapid development of this technology has not always allowed health issues to be addressed at the same speed. However, as is clearly evident from the last several days, there is an underlying awareness of the potential health hazards associated with this type of technology, and I believe as evidenced by all of you, there really is a commitment to deal with this health challenge.

Third, I don't think there's any question that composite materials can be manufactured and used safely using existing technology. That assumes, however, that there are really quality first-class occupational safety and health programs in effect in all those workplaces.

Fourth, I think it's apparent that much more should be done to inform workers of the hazards of using this type of technology and the precautions that they need to use in the workplace.

Fifth, workers need to be convinced that management and those who are charged with safety and health in the workplace are sincerely concerned about their welfare. This was exemplified by several statements that I heard, one of which was, "We want our employees to not only be protected, but to feel protected." Another comment that I heard was, "Plants with good management-employee relations will have less problems than those where the relations are poor."

My last overall observation is that we simply need to do a better job in getting that hazard information, those MSDSs, from the original supplier, through the distributor, through the manufacturer, to the ultimate user. And those MSDSs must contain the information that is supposed to be there, and it needs to be in a form that can be readily understood. That information must also be accessible. Health professionals, which many of you are, need to understand and step up to the obligation, to protect the disclosure of the proprietary information. This I believe is a workable problem.

As with any industry that has experienced quantum leaps in technology, there have been problems in ensuring worker health. But I think this conference has gone a long way in identifying those areas where we need to do some more work. I don't see these problems as insurmountable, either in terms of quantity or complexity. As Mr. Robinson said to Benjamin many years ago in the movie "The Graduate," he said, "Plastics, Ben, the future is in plastics." I think in our case, the future is now and the plastics of today are composites.

We must accept the challenge to deal with composites; we must resolve the problems and challenges that have been addressed and identified here in the last few days. And I trust that this task will be greatly simplified because of the new networks that have been established in the past few days, and the contacts that hopefully will bear a great deal of fruit in the future.

We're most grateful to all of you, and we thank you very much. Your contributions have been terribly, terribly important to making this work. And certainly you've helped the Air Force a great deal. Thank you very much.

Joseph C. Jackson

Executive Director
Suppliers of Advanced Composite Materials Association

I would be remiss if I did not reverse roles and thank Gary Vest and General Doppelt for giving SACMA, as well as AIA, the opportunity to participate in organizing this first-of-a-kind conference. I also want to thank and congratulate all the session moderators. They have been most helpful to me personally and quite tolerant of SACMA's ability to respond to their requests in a timely manner. Lastly, I would like to thank professionally those members of SACMA who were cajoled into speaking at the conference and then told they had approximately two weeks to prepare their remarks.

I suppose a pivotal question at this moment is....Where do we go from here? I would not like to think that this conference is the start and stop of constructive dialogue on the occupational health aspects of advanced composites. I know SACMA's Board of Directors believes it's but a start and that there will and should be a continuum of effort to address the problems and opportunities that face the advanced composite industry.

Candidly, to reiterate comments made by other industry speakers throughout the conference, SACMA's basic mission is to grow this industry. We want to grow it profitably. We want to grow safely. And we want to grow it cooperatively. Profitability is our responsibility. Currently, we are working through the Pentagon to get composite systems qualified quicker to improve profitability. Speaking to the health and safety issue, I should make note of another point made during the conference that some may have missed. SACMA for the past two and a half years has had a task force, under the able chairmanship of Dr. Charles Schwartz (Hercules), which has been working diligently to produce a white paper that will put into a single source document a compendium of the information SACMA members have on the safe handling/health effects of advanced composite materials. With fingers crossed, I believe SACMA will be able to release this document to the public by our annual meeting in April, or shortly thereafter. At least that's our present plan. We would certainly like to hear as well as honor any requests you may have for the document either directly through SACMA or indirectly through your respective organization.

That said, we're going to have to figure out collectively who picks up the baton relative to ongoing education and information exchange in this critical and changing arena.

In this regard, I would like to announce, couching in terms we use within our association, SACMA plans to be "proactive" rather than "reactive". This means sticking your neck out sometimes, but that's the key to getting on top of potential problems. Towards that end, and emanating from discussions held with AIA back in August, we recently reached agreement, in fact the attorneys are finalizing the paperwork, to form a joint working group with the Aerospace Industries Association. The mission of the working group will be to address health-related data needs as well as workable protocols for maximizing information exchange to minimize the risk to workers utilizing advanced composite materials. I believe this to be a bold step and major initiative from which we will all benefit.

I really don't have any more comments, except to invite George Tomer to the podium to extend his thanks on behalf of Dan Nauer and AIA.

Thank you.

George M. Tomer

Chairman, Occupational Safety and Health Committee
Aerospace Industries Association

I am George Tomer, the Chairman of the Occupational Safety and Health Committee for the AIA.

Since Dan Nauer, AIA Vice President, had to leave early, I felt it appropriate that we also, along with SACMA, address our thanks to all the participants for the opportunity to join with the Air Force in supporting this conference.

I would also like to thank all of the AIA members who participated in this outstanding conference and gave of their time and effort to share their views, both from their company's and, in many instances, their own personal experience perspectives. AIA and its member companies are definitely getting more active in Occupational Safety and Health matters, which might affect their employees.

In late August, AIA organized a special task force on composites. One of our goals is to work, as has been previously indicated by Joe Jackson of SACMA, on a combined industry effort. We feel that two industry associations and their member companies working toward a common goal of the health and safety of their employees is rather unique. We are also developing approaches for broadening our task force. As we have done here, we are talking with various people in organizations, companies, associations and various government activities that are involved in this area.

One observation that I would like to make, is that I feel this is but a small part of the entire hazard communication and chemical safety arena. Many of the underlying issues discussed during the last four days are consistent with what we are dealing in other activities in our companies. As we interchange information and experience, we are finding better ways to deal with the challenges discussed here.

We also feel that in our industry, we have the technical expertise, knowledge and a lot of good health and safety professionals to deal with the challenge and provide for a safe work environment for our employees. By working together, as has been done here, everyone benefits.

On behalf of the AIA and its companies' members, we thank you for the opportunity to participate.

. Major General Fredric F. Doppelt, USAF, MC

Commander, Human Systems Division (AFSC)
Brooks Air Force Base, Texas

I am extremely pleased with both the process and product of this timely interchange. The cooperative effort has been readily apparent throughout the week -- from the actual presentations -- through the late-night working group sessions.

There was a tremendous amount of behind-the-scenes work which may not have been apparent to the general audience. Each technical session had a working group made up of the session coordinator, each speaker, and other selected specialists who were tasked to condense a half day's presentations into a concise two-page summary of what we know and what we need to know in each area. These skull sessions have been a key productivity tool -- hammering out issues and formalizing consensus with each session.

This on-site assignment, combined with the short lead time for preparing the original presentations, made the participants' individual contributions especially significant.

I sincerely believe that the closer working ties fostered through this symposium will go a long way toward probing the unknowns and addressing remaining issues.

Stepping up to a strong and continuing industry-based forum in the future for addressing such concerns will be a vital link essential to our national defense posture.

An interesting observation is the rarity of a conference with representation from the particular blend of disciplines -- management, toxicologists, industrial hygienists, occupational physicians and labor -- such as we have had here. I trust that this cooperative, multidisciplinary approach will continue.

The panel discussions were lively, as expected. We must always feel free to air our professional opinions to make the most of the expertise represented here.

I would like to thank all of the participants for the extreme candor displayed both at the podium and in the panel discussions. This reflects a true spirit of cooperation and trust.

We began the first day with rather optimistic goals. Our success is readily apparent. We have addressed the issues, distilled the facts, and narrowed the focus on the remaining questions.

There are many who share credit for the obvious success of this conference. It was no small feat to bring together this talented group from such a diverse interest group. General DeHart of the Office of the Air Force Surgeon General, Mr. Dan Nauer of AIA and Mr. Joe Jackson of SACMA did a splendid job of rallying their forces to get this off the ground with so little advance notice.

Thank you for your efforts. I believe the results will provide a valued benchmark concerning the safe effective transition of this critical technology across the DoD and the aerospace industry.

APPENDIX

LIST OF ATTENDEES

Conference on Occupational Health Aspects of Advanced Composite Technology in the Aerospace Industry

February 6-9, 1989

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